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Advances in the study of piezoelectric polymers

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The literature review based on the works published over the last decade concerns the progress in research on innovative piezoelectric materials with current or potential practical applications. At the beginning, the nature of piezoelectric phenomenon is clarified. The main emphasis is put on presentation of polymers, biopolymers and polymer composites as well as hybrid materials with piezoelectric properties. Moreover, carbon nanomaterials are also included. These materials have recently become an intensively developing field, as evidenced by numerous scientific publications. Furthermore, the recently reported main methods of characterizations and selected examples of modern applications of piezoelectric materials in various fields (electronics, industry, medicine) have been discussed.
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1. Introduction

The intensive development of modern technologies in recent years is a big challenge for scientists working on new materials for various special applications. Among the sophisticated innovative materials, synthetic polymers play a significant role. They can be modified in a relatively simple way (both physically and chemically) and the technology of their production is well known and inexpensive. Polymeric electroactive materials including dielectrics with piezoelectric properties designed to microelectronics are

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becoming more and more important, as evidenced by a large number of scientific reports over the last decade.

The objective of this work is to present the recent results (with necessary references to previous key works) on piezoelectrics. Particular attention has been paid to polymers, biopolymers and polymeric composites exhibiting piezoelectricity. The most important properties of the presented materials, their advantages and disadvantages are discussed.

Although many studies on electroactive materials can be found in current literature, the distinguishing feature of this review is the collection of information on piezoelectric materials of various categories among which polymers form an especially important group. It should be pointed out that inorganic piezoelectrics can represent modifiers and fillers used as additives to polymer matrices to endow them with desirable properties. The polymeric composites obtained in this way are a promising and rapidly developing group of contemporary demanded materials. The selected works reveal current research trends in this field. With such approach, piezoelectric materials have not been described before.

Abbreviations:

ADP — ammonium dihydrogen phosphate,
AFM — atomic force microscopy,
CFE — 1,1-chlorofluoroethylene,
CNC — cellulose nanocrystals,
CNT — carbon nanotubes,
CTFE — chlorotrifluoroethylene,
CYTOP — cyclic transparent optical polymer,
CVC — current – voltage characteristic,
CVD — chemical vapour deposition,
DFT — density functional theory,
DMA — dynamic mechanical analysis,
DOS — density of states,
DSC — differential scanning colorimetry,
DTA — differential thermal analysis,
EGM — eggshell membrane,
FEP — fluoroethylenepropylene,
FE-SEM — field emission scanning electron microscope,
FGBS — fullerene – graphene bonded structure,
FTIR — Fourier-transform infrared spectroscopy,
GAg — graphene – silver nanocomposite,
GNDs — graphene nanodots,
HFP — hexafluoropropylene,
IMPC — ionic polymer – metal composites,
i-PP — isotactic polypropylene,
KPFM — Kelvin probe force microscopy,
LDPE — low density polyethylene,
LED — light-emitting diode,
LGS — lanthanum gallium silicate (langaze),
LLDPE — linear low density polyethylene,
MAP — magnetoactive polymer,
MDPE — medium density polyethylene,
ME — magnetoelectric properties,
MEH — mechanical energy harvester,
MEMS — microelectromechanical systems
MPB — morphotropic phase boundaries,
MWCNTs — multi-wall carbon nanotubes,
PA — polyamides/nylons,
PAN — polyacrylonitrile,
PC — polycarbonate,
PDMS — polymethyldisiloxane,
PE — polyethylene,
PEDOT — poly(3,4-ethylenedioxythiophene),
PET — poly(ethylene terephtalate),
PFM — piezoresponse force microscopy (piezoforce microscopy),
PI — polyimides,
PLLA — poly(L-lactic acid),
PMMA — poly(methyl methacrylate),
PNG — plasmonic nanogenerator,
poly(VDF-co-TrFE) — PVDF copolymer with VDF and TrFE units,
poly(VDF-ter-TrFE-ter-CFE) — poly(vinylidene fluoride-co-trifluoroethylene) copolymer with 1,1-chlorofluoroethylene units,
poly(VDF-ter-TrFE-ter-CTFE) — poly(vinylidene fluoride-co-trifluoroethylene) copolymer with chlorotrifluoroethylene units,
PP — polypropylene,
PSU — polysulfone,
PTFE — poly(tetrafluoroethylene),
PTrFE — poly(trifluoroethylene),
PVA — poly(vinyl acetate),
PVDF — poly(vinylidene fluoride),
P(VDF-TrFE) — poly(vinylidene fluoride-*co*-trifluoroethylene) (copolymer),
P(VDF-TrFE-HFP) — poly(vinylidene fluoride-*co*-trifluoroethylene) with HFP blocks,
PVGAg — GAg-doped PVDF hybrid nanocomposite,
P2VP-b-P(VDF-TrFE)-b-P2VP — poly(2-vinylpyridine)-*b*-poly(vinylidene fluoride-*co*-trifluoroethylene)-*b*-poly(2-vinylpyridine),
RGO — reduced graphene oxide,
SAXS — small-angle X-ray scattering,
SEM — scanning electron microscopy,
TEM — transmission electron microscope,
TFE — tetrafluoroethylene,
TFP — 3,3,3-trifluoropropene,
THV — polymer containing TFE, FEP and VDF,
TrFE — trifluoroethylene,
TSDC — thermally stimulated depolarized current method,
VDF — vinylidene fluoride,
XRD — X-ray diffraction analysis,
WAXS — wide-angle X-ray scattering,
ZONCE — cellulose-based composite with ZnO nanolayer.

2. Piezoelectric phenomenon

Piezoelectric phenomenon (or piezoelectric effect) is caused by the displacement of electric charges or alignment of molecular dipoles under the influence of applied mechanical force, which sometimes can generate the electric current. It occurs in solid materials that are insulators, *i.e.* dielectrics, in which electrical specific conductance should be below 10^{-8} – 10^{-10} S cm^{-1} (Refs 1 – 3). Piezoelectric materials often show the inverse effect, *i.e.*, deformation resizing due to the applied electrical pulse.[4,5] Such deformation is related to the generation of force and, as a result, the work is performed. As this phenomenon is reversible, such materials find a variety of practical applications provided that the piezoelectric effect is durable. Systems characterized by a permanent electric field are called electrets, by analogy to magnets exhibiting a constant magnetic field (this term is a combination of two words: electricity and magnet). Gene-

ration of an electric field is caused by permanent polarization of molecular dipoles or existence of permanent uncompensated electric charge in the bulk or at the surface of the material. Piezoelectric substances can be considered as intelligent materials (also referred to as smart materials) — under this term we mean systems that respond to external stimuli.

The piezoelectric effect was discovered by J. and P.Curie in 1880. However, the explanation of this phenomenon in connection with the material structure became possible only in the 20th century.[6–9]

It is impossible not to note several scientists who have brought a significant contribution to the development of the science of piezoelectrics, *e.g.*, Oliver Heaviside (Great Britain), Woldemar Voigt (Germany), Peter Debeye (Denmark – USA), Mototaro Eguchi (Japan), Georgi Nadjakov (Bulgary) and Vladimir Fridkin (Russia). The first practical applications of piezoelectric materials appeared during the World War I, while polymers with such properties found use much later, in the 1960s – 1970s.[6, 7, 10]

A necessary condition to create electrets is the anisotropy of the system. In such case the response obtained depends on the direction of applied stress (or axis of an electrical field). The piezoelectric effect occurs in crystalline materials with non-centrosymmetric crystal structure (the elementary cell has no centre of symmetry).[1–10] Among the known thirty two crystalline symmetry classes twenty of them include such structures.

The mechanism of formation of permanent electrets, and in particular the relationship between the structure of the material and its electrical properties appearing under the influence of stress has not been completely explained so far and is still the subject of an intensive research.

Preparation of permanently electrized material from dielectric polymers requires special treatment of samples, for example, action of strong electric field often at elevated temperatures, UV irradiation, ionizing radiation, charging with electrons ('charge injection'), corona discharge, chemical oxidation of surface or doping with specific substances. These factors can induce electronic, ionic, dipole or space-charge polarization in both polar and non-polar materials. In the context of the polarization method, electrets are mainly divided into three types: thermoelectres, photoelectres and radioelectrets.[11, 12] Other categories of electrets (electroelectrets, coronaelectrets, magnetoelectrets) are rarely found in the literature.

Ferroelectrics form a special class of piezoelectric compounds exhibiting spontaneous electrical polarization even in the absence of an electric field.[4, 13] Ferroelectricity generally occurs below a specific temperature, referred to as the Curie temperature (T_c), at which material becomes paramagnetic due to the phase transition. At temperatures above T_c, polarization completely disappears.

A related concept is flexoelectricity.[14–16] This effect is connected with spontaneous electrical polarization taking place in dielectric material under variable stress (or gradient stress). The difference between flexo- and piezoelectric effects lies in a variable tension as opposed to the constant stress causing electric polarization.

All ferroelectric substances are also pyroelectrics — the latter term means their ability to produce electric charges under the influence of temperature changes.[17]

Electrets can be produced not only in the form of solids, but also liquids, as exemplified by charged droplets generated by electrospray ionization during mass spectrometry analysis.[18–20] Such materials are called ionic electrets.

It should be pointed out that the properties and durability of piezoelectric materials depend not only on their chemical structure but also on the method and conditions of their manufacturing.

3. Theoretical bases

The theoretical background of the piezoelectric phenomenon was the subject of many previous monographs and textbooks as well as contemporary works.[6–8, 10–13, 21–27]

Equations describing the piezoelectric effect take into account the coupling of the electric field (E_k) and mechanical parameters [stress (T_{ij}) and strain (S_{kl})].[17, 28]

$$T_{ij} = c^{E}_{jkl}s_{kl} - e_{kij}E_k \tag{1}$$

$$D_i = e_{ikl}S_{kl} + \varepsilon^{S}_{ij}E_k \tag{2}$$

where D_i is the electric displacement, c^{E}_{ijkl} is the elastic constant (superscript indicates that the electric field is constant), e_{ikl} is the piezoelectric constant, ε^{S}_{ij} is the dielectric constant (at constant strain). The stress (T_{ij}) and the electric displacement (D_i) are independent variables.

The piezoelectric effect depends on the relative directions determined on the basis of the polarization direction of the piezoelement. The reference axis number 3 is an axis parallel to the direction of polarization (in the case of films, perpendicular to the film surface).

Most often, the parameters characterizing piezoelectric properties of anisotropic materials are piezoelectric charge constant d_{3n} and piezoelectric voltage constant g_{3n} expressed as:[6, 7, 17]

$$d_{3n} = \frac{q}{P_n} = \frac{Q}{F} \tag{3}$$

$$g_{3n} = \frac{U}{P_n d} \tag{4}$$

where Q is the generated charge, A is the surface of the electrode, q is the charge density, F is the force acting on electrets, n is the direction of the acting force, U is the generated voltage, P_n is the stress in determined direction of the acting force, d is the film thickness.

Dependence of mechanical and electrical properties of solid materials is clearly described by the Heckmann diagram representing the mechanical, electrical and thermodynamic properties in the form of a triangle.[27, 29–33] This diagram shows the relationship between three physical factors: mechanical stress (σ), electric field (E) and temperature (T). These factors are closely related to next three parameters, namely, strain (ε), dielectric displacement (D) and entropy (S), which are in turn directly connected to compliance (s), permittivity (e) and heat capacity (C) (Fig. 1).

As previously mentioned,[7, 11] the properties of piezoelectric solids are determined by the polarization capability and the accumulation of volume electric charges (so-called entrapping of current carriers) and their transport in a material.

The polarization capacity can be described by the dipole moment (μ) of a molecule and the dielectric permittivity (e)

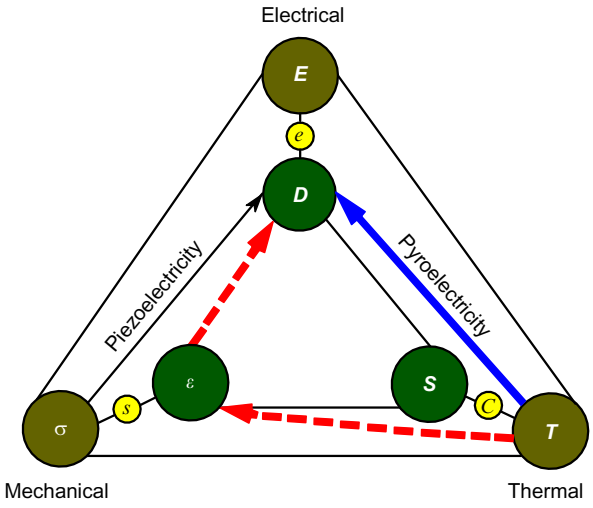


Figure 1. A Heckmann diagram illustrating the thermodynamically reversible interactions that may occur among the thermal, mechanical, and electrical properties of a crystal.[33]

[or relative permittivity (κ)], which is related to dielectric susceptibility (χ). Polarization (P) is proportional to electric field intensity (E) (Refs 6, 7)

$$P = \varepsilon_0 \chi E \quad (5)$$

where ε_0 is the dielectric constant. The electric displacement (D) is expressed as

$$D = \varepsilon_0 E + P \quad (6)$$

The transport of electric charges in inorganic dielectrics is possible due to electron transfer from the valence band to the conduction one after providing sufficient energy to overcome the energy gap. In ionic substances the charge is transferred by ions. However, in the polarization phenomenon, it is also necessary to consider the orientation and spatial-charge mechanism. The latter is associated with the accumulation of charges at the interface in heterogeneous systems (also called migration or interlayer mechanism). It is typical of polymeric systems.

In spite of the fact that polymer electrets have been known for many years, the studies thereof are still in progress because the mechanism of electro-coupling in these materials remains unclear.[12, 34]

In the case of macromolecular compounds (such as semicrystalline polymers), the formation and movement of carriers is strictly related to the presence of various defects (those in chemical structure, conformational irregularities, surface imperfections in crystallites, dislocations, voids, electron/ion traps, admixtures of different types, *etc.*). It is generally accepted that mechanism of hopping of charge carriers in the polymeric materials is prevailing.[35]

However, these naturally occurring charge carriers are characterized by insufficient mobility due to their immobilization in low-energy traps. Only the injection of charge in the poling process leads to a significant change — these excessive charges can immediately appear in the conductive band or can be activated at elevated temperatures. The description of dielectrics in the electric field requires consideration of both electrical conductance and energy dissipation processes. The injected charge is called 'external polarization'. The initially achieved polarization gradually decreases due to the particle displacement in certain time [relaxation time (τ)].

Recently de Jong *et al.*[27] published the results of calculations of piezoelectric tensors for about a thousand compounds, and the theoretical values for selected materials were compared with experimental data. This provided an extensive database, and also such approach makes it possible to design and develop the structure of piezoelectric materials for specific practical applications basing on a computational quantum mechanical modelling.

4. General information on types of piezoelectric materials

The piezoelectric effect occurs in both inorganic and organic materials, and current studies, similar to previous ones, concern these both groups of chemical compounds.

Although the present review is devoted mainly to piezoelectric polymers, but nowadays, inorganic materials (natural minerals or ceramics synthesized on a large scale) are often used as modifiers added to polymer matrices. The following examples of such additives can be listed: quartz (SiO_2), topaz [alkaline aluminium fluorosilicate $Al_2SiO_4(OH,F)_2$], tourmalines [silicates $XY_3Z_6[(OH)_4(BO_3)_3(Si_6O_{18})]$ where X = Na; Y = Fe, Mg, Ca, Mn, Li, Al; Z = Al, Fe], ammonium dihydrogen phosphate [ADP, $(NH_4)H_2PO_4$], Seignette's salt (potassium tartrate, $NaKC_4H_4O_6 \cdot 4\,H_2O$), langaze (LGS, lanthanum gallium silicate, $La_3Ga_5SiO_{14}$), perovskite [calcium titanate(IV), $CaTiO_3$], tungsten bronze, *e.g.* Na_xWO_3, where $x \leqslant 1$, as well as $Sr_{1-x}Ba_xNb_2O_6$, $x = 0.60$ or 0.50; $Pb_{1-x}Ba_xNb_2O_6$), PZT ceramics [zirconate and lead titanate, $Pb[Zr_xTi_{1-x}]O_3$ $(0 \leqslant x \leqslant 1)$] as well as PLZT ceramics [a mixture of zirconate and lead titanate modified with lanthanum oxide, $(PbLa)(ZrTi)O_3$].[36, 37]

Inorganic materials mentioned above are generally characterized by good piezoelectric properties[38 – 47] but also have some disadvantages and technological limitations. The most important ones include the poor molding capacity, insolubility in organic solvents, limited size and high brittleness in many cases. This is the reason for a search for new piezoelectric materials.

5. Carbon nanomaterials

A very promising group of modern piezoelectric materials comprises carbon with nanometric dimensions. These materials based on various allotropic forms of carbon (fullerenes, graphene/graphene oxide, carbon nanotubes and nanofibers) became very important in materials science and technology during the last decades due to their unique properties.[48 – 54] The impetus for research of nanocarbon structures[55 – 57] was given by the Nobel Prize in chemistry awarded to H.W.Kroto, R.F.Curl and R.E.Smalley in 1985 for their research on fullerenes and the possibilities of their production on a scale exceeding the laboratory one. The Nobel Prize in physics awarded to A.Geim and K.Novoselov in 2010 for key graphene studies also influenced intensive interdisciplinary researches on this group of materials.

Knowledge about carbon nanomaterials contributes to the rapid development of nanotechnology, which allows

manipulations at the atomic level. Produced nano-sized structures (< 100 nm) enable further miniaturization of electronic equipment. Currently, fullerenes are widely used in microelectronics, optoelectronics, photovoltaics, energy industries as well as in diagnosis and sensing in medicine because they do not show toxic effects on living organisms, which cannot be said about carbon nanotubes.[58] Also, graphene, carbon nanotubes and nanofibres are very promising materials for similar uses.[59, 60]

Application of nanomaterials in bio-nanotechnology is possible due to interdisciplinary research of physicists, chemists, biologists and doctors. Fullerene-C_{60} has been described as one of the main starting materials to produce selective and sensitive biosensors (*e.g.* sensors of glucose or urea), which can replace traditional sensors of the previous generation.[61] Undoubted advantages of fullerenes include their nanometric size, morphology and physicochemical properties, which are influenced by hybridization of carbon atoms (sp^3 and sp^2). Presence of unsaturated carbon bonds allows for easy functionalization of spherical molecule surfaces in reactions of nucleophilic or radical addition as well as cycloaddition. The possibility of biomolecules or organic ligands (*e.g.* proteins, enzymes, DNA) to be immobilized on C_{60}-fullerene molecules *via* adsorption or covalent bonding, opens new horizons in biotechnology.[61, 62] It was suggested that (C_{60})–DNA hybrids can be novel nano-biomaterials with potential application as gas sensors, catalysts, electronic and optical devices or sensitive biosensors, as examplified by DNA bonded onto a fullerene impregnated electrode for detection of *Escherichia coli* bacteria.[63]

Also, the production of C_{60}–antibody-coated piezoelectric sensor, based on C_{60}–anti-human IgG and C_{60}–anti-haemoglobin is reported.[61, 64] Studying such material explained the mechanism of interaction between C_{60} and the antibody. The change in crystal resonant frequency, related to the deposited mass, was investigated. Moreover, the effect of an antibody concentration, pH and temperature on sensor response has been found. This system was also developed to detect haemoglobin in aqueous solutions.[64] However, it was pointed out that the practical applications are still limited and further studies are necessary.[61]

A novel carbon nanomaterial, called button-like structure, was obtained by adsorption of the C_{60} molecules onto a graphene sheet (Fig. 2).[65] This fullerene–graphene bonded structure (FGBS) exhibited both semiconducting (mainly due to graphene) and piezoelectric properties. The structure of FGBS was elucidated and confirmed by calculation of the density of states (DOS).[66]

It has been proved that sp^2 hybridization was locally distorted due to the graphene–fullerene interactions. In other words, π-bonds were consumed in the process of connection of both substances. At the junction, the carbon atoms adopted mixed sp^2-sp^3 hybridization. As a result, a band gap appeared, whereto the carbon atoms around the graphene–fullerene connection contribute mainly. Applying the mechanical force along the graphene–fullerene bonding direction (pressure on the fullerene button) caused a piezoelectric effect. However, at larger strain (above 20%; 20% stress corresponds to 0.0057 eV $Å^{-1}$) the band gap disappeared and the material became a conductor. Due to these extraordinary electric properties, FGBS were proposed to be used as nanobuttons or force/presure sensors in future equipment for various purposes.

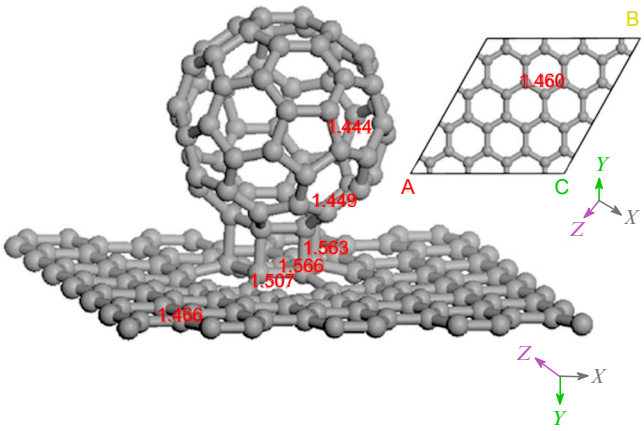


Figure 2. Atomic structure of C_{60}–graphene bonded structure with the bond length indicated.
The graphene sheet is shown as an inset.[65]

Some of the latest works described the preparation of graphene with piezoelectric and flexoelectric properties.[15, 67] Graphene, being a carbon layer of monoatomic thickness, consists of six-membered rings, and is often referred to as a honeycomb structure. It is a good electronic conductor similar to metals, as well as very strong and flexible, but it does not exhibit piezoelectric properties because of the lattice symmetry. Nevertheless, these properties can be generated disturbing the regular structure of graphene by introducing defects, impurities or modifiers. Javvaji *et al.*[15] used the classical molecular dynamics to determine the electromechanical coupling in defected graphene. The different shapes of defects (circular, triangular and trapezoidal) have been considered and such structures were compared to pristine graphene. Charge–dipole potentials were calculated and the stress–strain response was analyzed. It was concluded that circular symmetric deformation does not induce the graphene piezoelectricity, contrary to triangular and trapezium-shaped defects. This approach to modify graphene by breaking its symmetry can be used in production of novel electromechanical devices.

Another work demonstrates that graphene piezoelectricity can be induced by chemical doping, which also leads to breaking its inversion symmetry.[67] This can be accomplished by embedding additional atoms (adatoms) on one side of the graphene layer. Ong and Reed[67] calculated piezoelectric coefficient using the density functional theory (DFT) method for graphene doped with Li, K, H and F atoms. In addition, the mixture of atoms of two elements (H + F and Li + F) was examined. In all cases, the inversion symmetry is broken, thereby piezoelectric properties are generated. Theoretical calculations showed that Li and K atoms are preferably placed inside the rings and graphene doped with both these alkali metals has the highest piezoelectric coefficient. The effect of dopant concentration or, strictly speaking, surface coverage by added lithium atoms has also been studied. It was revealed that the highest piezoelectricity occurs in graphene, in which one Li atom falls on eight carbon atoms. However, the position of adatoms has practically no effect on the piezoelectric response. The values of piezoelectric coefficients calculated

for graphene with adsorbed atoms are comparable to those for other known piezoelectrics. The obtained piezoelectric graphene can contribute to the development of 2D electromechanical devices such as nanosized actuators, motors, robots, *etc*.

Piezoelectric properties of carbon nanotubes (CNTs) have been studied by Ageev and coworkers[68–70] using combined techniques of scanning probe microscopy.

In the beginning of their study, the model of the resistive switching in vertically aligned carbon nanotube has been proposed.[68] The processes of nanotube deformation, polarization and piezoelectric charge collection were discussed. For experimental work, CNTs obtained by plasma-enhanced chemical vapour deposition, were extracted from support by mechanical force lithography. Current–voltage characteristic (CVC) was measured applying changing voltage pulse of 1.5 V. The structure resistance significantly changed under the action of an external electric field, suggesting the resistive switching effect (switching time is 13 ps). Theoretical and experimental results are consistent and promise the use of vertically aligned CNTs in the future nanoelectronics devices (*e.g.* as the nonvolatile resistive random-access memory with ultra-high speed and density).

In their next study, the similarly obtained multi-walled CNTs were described.[70] Scanning the surface by the atomic force microscopy (AFM) tip caused the formation of non-uniform strained CNT bundles as a result of van der Waals forces. Surface potential and current voltage of strained CNTs were measured to determine their piezoelectric properties.

The development of these studies included measuring the piezoelectric response in CNTs subjected to bending and compressive strains (Fig. 3). The current generated by an individual nanotube was 24 nA and the surface potential ranged 268–110 mV. It was shown that the surface potential depends on the magnitude and type of strain as well as on the diameter of nanotube bundles. The maximal value of piezoelectric current was observed in the case of longitudinal compression or stretching. It was concluded that this may be caused by the formation of a dipole nanotube wherein the charges accumulate at its ends. Moreover, it was pointed out that strain acted on CNTs generates not only piezoelectric effect but also change their band gap and conductivity.

These works are part of a new field called nanopiezotronics, pioneered by Wang.[71,72] Nanopiezotronics concerns coupled piezoelectric and semiconducting properties

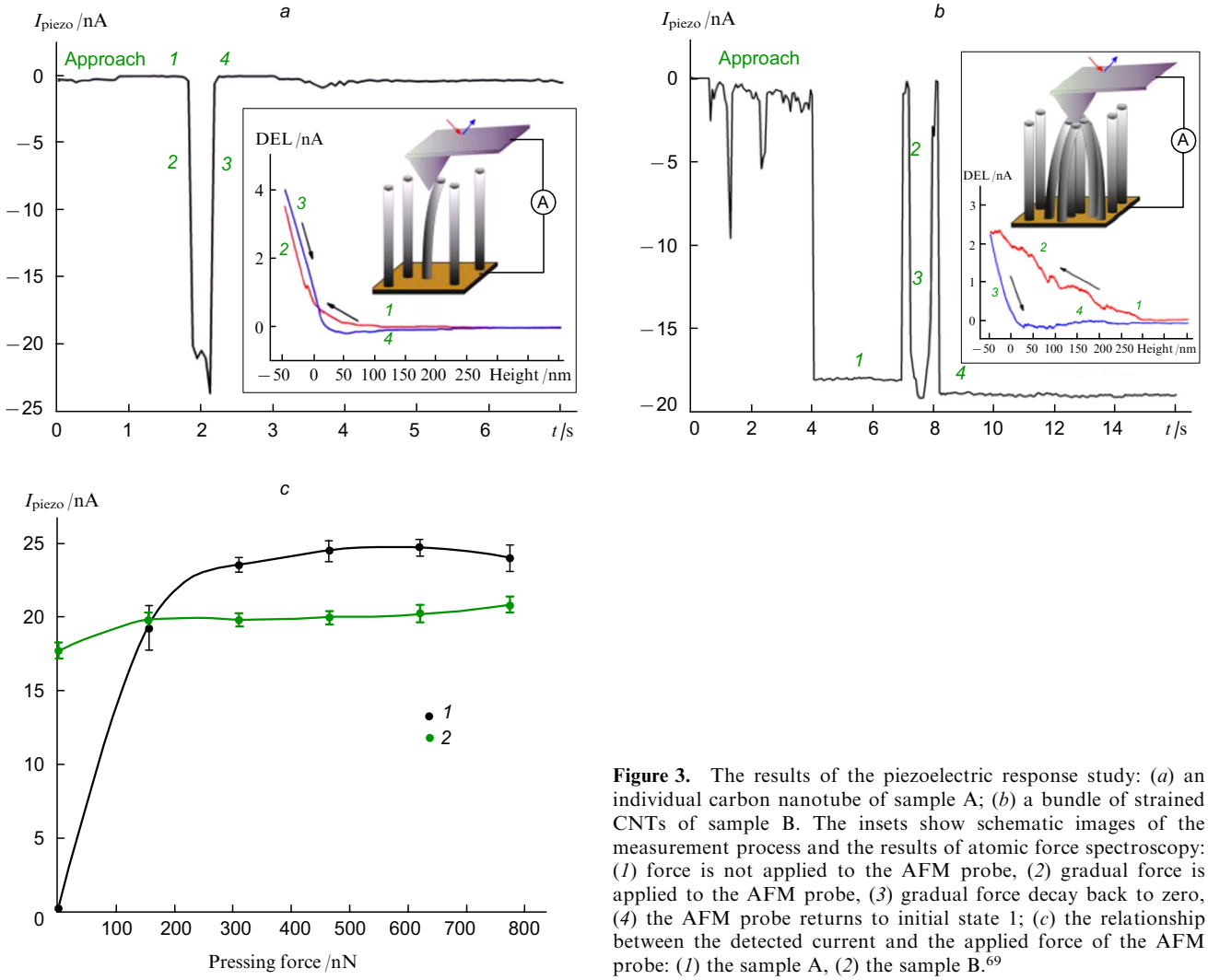


Figure 3. The results of the piezoelectric response study: (*a*) an individual carbon nanotube of sample A; (*b*) a bundle of strained CNTs of sample B. The insets show schematic images of the measurement process and the results of atomic force spectroscopy: (*1*) force is not applied to the AFM probe, (*2*) gradual force is applied to the AFM probe, (*3*) gradual force decay back to zero, (*4*) the AFM probe returns to initial state 1; (*c*) the relationship between the detected current and the applied force of the AFM probe: (*1*) the sample A, (*2*) the sample B.[69]

of nanomaterials invented for fabrication of electronic devices such as nanogenerators, sensors, transistors and diodes.

Finally, it should also be noted that carbon nanomaterials are valuable modifiers for making polymer composites with piezoelectric properties.

6. Synthetic polymers with piezoelectric properties

Disadvantages of inorganic piezomaterials can be eliminated in polymer systems with piezoelectric properties. This is the reason for the dynamic development of such materials that combine features of organic and inorganic substances; hence, they can be designed for many specific applications in modern technologies and microelectronics. An undoubted advantage of polymers is also the possibility to modify their chemical structure and to obtain multifunctional materials.[73 – 80]

Polymeric piezoelectrets can be obtained in any shape and size, for instance in the form of thin films or cables, using conventional processing technology. Such materials have all typical advantages of polymers — they are flexible, lightweight and resistant to various factors (elevated temperatures, water, chemicals, oxidative agents, environmental impurities, UV radiation, mechanical forces, ageing, *etc*.).

A lot of various polymers and copolymers (both amorphous and semicrystalline) exhibiting piezoelectric properties have been described in literature: poly(vinylidene fluoride) (PVDF);[12, 81 – 84] poly(tetrafluoroethylene) (PTFE);[85] poly(ethylene terephthalate) (PET);[85] polymethyldisiloxanes (PDMS);[86] polyamides/nylons (PA);[87] polyimides (PI);[88] polyacrylonitrile (PAN);[89] polyolefins,[90] PVC;[91] poly(vinyl acetate) (PVA);[91] polyurea,[92] epoxy resins, and even poly(methyl methacrylate) (PMMA), polysulfones (PSU) or polycarbonates (PC).[11] Not all of the above polymers have found practical applications but they may have great potential in future. Improving the stability of polymer electrets and preventing relaxation processes causing discharging is an important challenge in this field.

Polymers of different morphology exhibit piezoelectric effect.[79] They are amorphous and semicrystalline polymers, composites built of polymer matrix with embedded particles or fibres as well as polymers with cellular structures containing air voids (cavities) where electric charges can accumulate. The piezoelectric composites can be obtained by blending a non-piezoelectric polymer with piezoceramic fillers of different size and shape.[79] The structure of such piezoecomposites depends on the interactions between macromolecules and a particulate filler, which can form dispersed separate phase or can be partially mixed with a matrix. The cellular polymers (also called voided polymers) can be obtained by using a foaming agent in processing or stretching (orientation) of extruded films.

Another possibility is a multilayer (laminated) structure.[79] Randomly distributed dipoles should be properly oriented, which can be accomplished during the poling process under the constant electric field or corona discharges. The dipoles are usually formed at elevated temperature, thus, they are 'frozen' after cooling the sample to the room temperature.

Such polymers generally suffer from small piezoelectric coefficients compared to ceramic piezoelectrics (which can reach values > 100 C/N), thus, except PVDF, they still have no practical meaning. However, an appropriate modification of the polymeric matrices allows for a significant improvement of their piezoelectric parameters.

6.1. Poly(vinylidene fluoride)

Among the piezoelectric polymers, PVDF has been retaining the leadership for years. It is one of the few macromolecular compounds that has already found application as a piezoelectric material but has been still the subject of intensive research in recent years.[12, 81 – 84, 93 – 96]

Poly(vinylidene fluoride) is a crystallizable polymer with a relatively simple chemical structure (there are two fluorine atoms at every second carbon atom in the hydrocarbon backbone). The crystallization degree of PVDF often exceeds 50%. Usually, it exists in the most stable, nonpolar α form — $TGTG'$ (where T and G are *trans*- and *gauche*-conformations), wherein the fluorine atoms are arranged alternately on both sides of the hydrocarbon chain, and does not exhibit piezoelectric effect.[77]

The situation changes in the β form (*TTTT*, all-*trans*), in which the fluorine atoms are located on the same side of the chain, resulting in the permanent dipole formation. The mutual isomeric transformations caused by chain rotation are possible at elevated temperature, during drawing, melt quenching or crystallization from solution under strictly defined conditions.[84]

Other crystalline structures in PVDF, methods of their identification and possibilities of obtaining β phase, most interesting from technological point of view, were reported by Martins *et al*.[96] A detailed analysis of α→β and α→γ phase transformations and their kinetics has been performed using quantitative Fourier-transform infrared (FTIR) spectroscopy.[97]

The piezoelectric coefficient of PVDF (d_{33} = 13 – 28 pC/N;[79] d_{31} = 12 – 23 pC/N (Ref. 80) is higher than in other polymers but lower than in ceramic piezoelectrics. In addition to piezoelectric properties, PVDF is also characterized by ferroelectricity and pyroelectricity.[84, 96] The presence of the most electronegative element, fluorine, causes a dipole moment of up to 5×10^{-30} Cm in repeating units and relatively high dielectric constant (~8.4 – 20), which can be further increased by incorporation of suitable inorganic modifiers.[84, 98, 99]

Theoretical calculations using quantum chemistry methods provide somewhat different piezoelectric values for modelled β-phase PVDF.[100] However, these data are in good agreement with results in nanoscale obtained using atomic force and piezo-response force microscopy. It was found that d_{33} was in the range from −16.6 to −19.2 pC/N for dielectric permittivity e = 5 while for e = 10 it ranged from −33.5 to −38.5 pC/N. The coefficient d_{31} was *ca*. 15.5 pC/N at $e \approx 5$.

The negative piezoelectric effect detected in this case was caused by redistribution of electronic molecular orbitals, leading to the displacement of atomic nuclei and reorganization of total charges under an electric field.

Owing to tremendous progress in the scanning electron microscopy in recent years it became possible to visualize material structure at atomic resolution (even below 0.05 nm). This can be exemplified by the aberration-corrected transmission electron microscopy, which proved to be a very useful method to determine the morphological structure of PVDF at atomic level.[101] It was possible to observe locations of atoms in segments in PVDF nanofibres

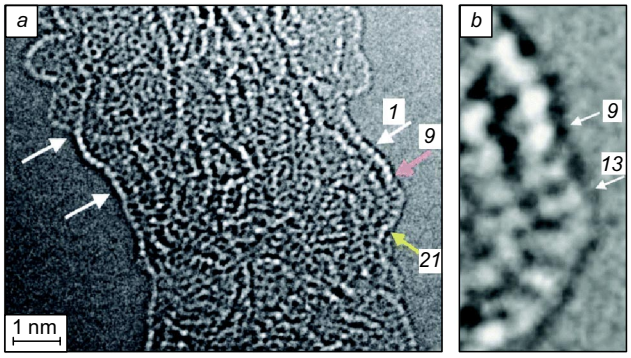


Figure 4. High resolution transmission electron microscope image of a thin nanofibre of PVDF (*a*), a magnification of part of (*a*) (*b*). The brightest dots (indicated with white arrows) were attributed to view directions along a line between two fluorine atoms bonded to the same carbon atom. The segments on the surface of nanofibres (indicated on the right side), in which subsequent atoms were numbered, were chosen for molecular modelling to confirm the structure interpreted in microscopic images.[102]

(in particular conformations) as well as morphology changes caused by the segment movements such as twisting around the molecular axis [102] (Fig. 4). It was found that the rows of CF_2 groups appeared at 0.25 nm intervals and the distance between two fluorine atoms attached to the same carbon atom was 0.2 nm. Molecular dynamic modelling based on high resolution TEM images confirmed the described structure of PVDF. Detailed studies of macromolecules conformations allow one to establich a correlation between the structure and piezoelectric properties of PVDF and its copolymers.

This thermoplastic fluorocarbon polymer is non-flammable, chemically and thermally resistant, photostable, resistant to abrasion, easily obtainable by traditional processing methods (injection, moulding) and having a low density (1.78 g cm^{-3}). Therefore, it is applied not only in the electronic industry but also as automotive components, protective coatings, membranes, pipes for the chemical and petrochemical industry, polymer processing aids.[12] Moreover, PVDF and its copolymers, similarly to other functional fluoropolymers, can be used for proton exchange membrane fuel cells.[84]

Detailed research of the time-dependent electrical and mechanical response of PVDF in the form of a thin film under various loadings and temperatures revealed that in this case theoretical description of piezoelectricity has some shortcomings.[103] Here, the mechanical properties have been studied by static tests, quasi-static creep tests and dynamic oscillatory investigations of commercially availale PVDF films of 28 μm thickness. Moreover, the model of polarization and dielectric relaxation has been proposed. Modelling makes it possible to predict a polymer behaviour for a longer time scale. The results led to a conclusion that the linear viscosity theory describes well a time response of PVDF at the applied stress below 57% in the material direction 1 (where responce direction of polymer film is parallel to the direction of aligned chains) and below 75% in material direction 2 (direction perpendicular to aligned macromolecules). Beyond these limits, the nonlinear viscoelastic law should be applied. The strong dependence of temperatures and cyclic frequencies on response of PVDF has also been proved.

Poly(vinylidene fluoride) is widely used to construct various types of sensors. Combination of good piezoelectric properties of the polymer and its flexibility allows application of such sensors where brittle and rigid ceramic materials are not suitable.

The greatest expectations arouse in the field of PVDF applications as energy harvesters.[77,104] The energy produced by body movements (walking, running, gymnastics, going up the stairs) can be transformed to electrical energy and used in sensors for health monitoring.[105] Such transducers in the form of thin flexible films can be placed directly on the human body or embedded in clothing. The obtained voltage output (V) can be calculated according to the formula [105]

$$V = \frac{t}{\varepsilon} d_{31} Y \frac{\Delta l}{l} \qquad (7)$$

where t is the film thickness, ε is the absolute permitivity of the material, d_{31} is the charge piezoelectric coefficient, Y is the Young modulus and $\Delta l/l$ is the elongation of polymeric film. The first subscript in d_{31} refers to the electrical axis (thickness axis), while the second one refers to the mechanical axis (which can be 1, 2 or 3 because the force can be applied in any direction). In fact, the high voltage output is generated when the force is applied along the sample (*i.e.* in direction 1).

The value of the power output measured in this experiment ranged as 0.1–10 μW depending on the particular place of contact with the body. A wearable sensor seems to be very practical, comfortable, cheap and non-invasive. In addition, the measured pulse can be sent to proper devices such as PC or smartphone (*e.g.* into the health centre).

The PVDF-based energy harvester was also proposed by Ennawaoui *et al.*[106] It was proved that PVDF is a material suitable for production of intelligent road equipment used both for energy acquisition and for measuring the vehicle speed. The absorbed energy can be applied to make independent energy sensors. The proposed system, called smart speed bump (SSB), is composed of piezoelectric material (PVDF), steel springs and converter based on electronic circuit, which can be used to store a current in a battery or supply a wireless sensor. The role of spring is to absorb energy under loading connected with distortion and slow releasing when returning to the original shape. This SSB is inexpensive and can generate a power above 4 mW cm^{-2} with 0.75% strain at 13 Hz. Energy recovery from car traffic (particularly during crossing the retarding bumps) can be a valuable contribution to sustainable energy development.

The innovative solution of manufacturing of piezo/pyroelectric devices based on PVDF has been proposed by Mojati-Talemi *et al.*[107] using vapour phase polymerised (VPP) poly(3,4-ethylenedioxythiophene) (PEDOT) — a conductive polymer — as a flexible electrode overlay material. Air plasma treatment and VPP were found to provide better adhesion of both polymers and improved mechanical properties compared to PVDF system with platinum electrode. The plasma action led to an increase of the surface energy due to oxidation, confirmed by contact angle measurements. This modification led to a significant increase of piezoelectric output voltage. When heating the

system to 50 °C above ambient, pyroelectric voltage outputs were obtained. This system can be used to generate current through the energy of human inhalations and exhalations.

In his Doctoral Thesis, Gusarov [108] considered PVDF in the context of obtaining electricity from heat using both piezoelectric elements and shape memory materials (NiTiCu alloy). In addition to PVDF characteristics and piezoelectricity principles, the technology of production of thermal energy harvesting device is described. Results of measurement of piezoelectric properties under variable electric fields, temperatures and strains are presented. Power management circuit was designed and integrated with the PVDF piezoelectric. A wide range of applications, including flexible wireless sensors, has been proposed.

Recently, the piezoelectric textile structures based on 100% PVDF containing mainly β-phase (up to 97%) were described.[109] Poly(vinylidene fluoride) yarn was produced by melt spinning and used for 2D and 3D weaving of fabrics. The optimal crystallinity was obtained by the mechanical stretching. In this work, the degree of crystallinity was determined by differential scanning colorimetry (DSC), while the content of β-phase [$F(\beta)$] was calculated from FTIR spectra:[109]

$$F(\beta) = \frac{A_\beta}{1.26A_\alpha + A_\beta} \quad (8)$$

where A_α and A_β are absorption bands at 766 cm^{-1} and 840 cm^{-1} corresponding to α and β phases, respectively. To determine the output voltage during compression, Dynamic Mechanical Analysis (DMA) was employed. It was found that maximal electric voltage applied during the poling process of 2D and 3D fabrics was the same despite the significant difference in thickness. This suggested that the porosity (not the thickness) is the decisive factor (which is the same for 2D and 3D fabrics). The obtained output voltage (2.3 V) for 3D weave is 16 times greater than that for the 2D one. Proposed textiles can act as power-generating systems applying human work transported through shoes and seats.

6.2. Poly(vinylidene fluoride) copolymers and terpolymers

Current scientific studies also concern electroactive copolymers and terpolymers based on fluoropolymers. In the review by Soulestin *et al.*[110] the issues related to the synthesis, structure and properties of poly(VDF-*co*-TrFE), where VDF is vinylidene fluoride and TrFE is trifluoroethylene unit, are discussed in detail. Copolymers containing 50 mol.% – 80 mol.% of VDF easy crystallize in the β form, which provides favourable electrical properties. Particular attention was given to microstructure of copolymers depending on the polymerization type and conditions. The changes in crystalline phase caused by annealing and poling were presented. Copolymer was characterized by the Curie transition temperature being lower than the melting point, good thermal stability and better solubility in organic solvent compared to PVDF. The dielectric constant was maximal at 60/40 VDF/TrFE molar ratio. The piezoelectric coefficient of poly(VDF-*co*-TrFE) was also effected by the component ratio as well as by the crystallinity degree.

Furthermore, PVDF/TrFE/TFE copolymers showed a transition to a paraelectric phase at elevated temperatures.[92] It is worth noting here that the paraelectric material, although undergoing polarization under the influence of an electric field, loses its polarity when the field is removed. In other words, such material has no permanent electric dipole.

Nunes-Pereira *et al.*[93] also reported this kind of copolymers. The possibility to prepare piezoelectric materials based on P(VDF-TrFE) in an environmentally friendly manner was emphasized because of using non-toxic 1,3-dioxolane instead of typically applied *N*,*N*-dimethylformamide.

Theoretical modelling of PVDF, poly(trifluoroethylene) (PTrFE) and poly(vinylidene fluoride-*co*-trifluoroethylene) [P(VDF-TrFE] copolymer was used to calculate energy of conformers.[111] The lowest energy was found for *trans-gauche – trans-gauche′* (*TGTG′*) conformation of PVDF, contrary to PTrFE, where the all-*trans* (*TTTT*) structure was preferred. This result was explained by an increased intramolecular repulsion between the fluorine atoms as well as by an increased intermolecular attraction during copolymerization.

Phase changes in P(VDF-TrFE) films under the electron beam irradiation were studied by micro-Raman scattering measurements, X-ray diffraction analysis and FTIR spectroscopy.[112] It was observed that both crystalline phases (α and β) co-exist independently of the electron beam operation, but the temperature dependencies of α and β phases are different. At temperatures where the polar nanoregions disappear, the α/β phase ratio increases rapidly.

In ferroelectric P(VDF-TrFE) copolymers morphotropic phase boundaries (MPB), similar to those in perovskites, were obtained by the proper tailoring of the tacticity.[113] Such boundary joining two competing phases with distinct symmetries enhances the transfer of mechanical to electrical energy and *vice versa*. It is connected with simultaneously occurring ferroelectric and relaxor properties. Usually, MPB formation results from the transition between tetragonal and rhombohedral systems caused by compositional changes or mechanical pressure. In the above terpolymer, the chain tacticity played a dominant role in structural competition between the *trans*-planar and 3/1-helical phases, responsible for high piezoelectric coefficient (−63.5 pC/N).[114]

Terpolymers composed of three different units are characterized by even more complex structure that significantly affects the material properties as exemplified by terpolymer poly(VDF-*ter*-TrFE-*ter*-M) (where M is the third unit).[84] The monomer M can be a chlorinated compound such as vinyl chloride, chlorofluorinated compounds (with 1 – 3 F atoms) or others. The most studied termonomers are 1,1-chlorofluoroethylene (CFE) or chlorotrifluoroethylene (CTFE).[84] Poly(VDF-*ter*-TrFE-*ter*-CFE) and poly(VDF-*ter*-TrFE-*ter*-CTFE) exhibit a relaxor-ferroelectric behaviour (RFE) connected with formation of crystalline nanodomains with small number of aligned dipoles, sensitive to electric stimuli. Both terpolymers have much higher dielectric constant (about 80) than PVDF (12) at room temperature and 1 kHz. Moreover, the structure and properties (including electroactivity) of the above-mentioned copolymers and terpolymers can be modified *via* crosslinking using chemical, radiation or photochemical methods as well as *via* grafting process.

Copolymerization of VDF, TrFE and 3,3,3-trifluoropropene (TFP) has been investigated.[110] Monomer reactivity ratios were determined by Kelen – Tudos method while the microstructure of obtained terpolymers was elucidated

by ^{1}H and ^{19}F NMR spectroscopy. Moreover, research of thermal transitions, thermal stability and electroactivity was used to draw structure–property correlations of the poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers.

As mentioned above, relaxor ferroelectric (RFE) polymers represent a specific type of materials, in which nanosized domains are formed. Currently, there are mainly random terpolymers containing Cl atoms in one type of units, *e.g.*, poly(vinylidene fluoride-*co*-trifluoroethylene-*co*-Cl).[115] Being chlorine-substituted, this polymer is unstable at elevated temperatures promoting dechlorination, which limits its processing. The authors proposed chlorine-free terpolymers P(VDF-TrFE-HFP) where HPP is hexafluoropropylene. The introduction of HPP blocks disrupted crystallization, but mechanical stretching led to the ordering, necessary to form ferroelectric domains. As it turned out, the durability of ordering and ferroelectric properties of HPP ensured annealing at temperatures above the Curie point under tension. It was emphasized that the nature of transitions between nanodomains in such polymers and their effect on ferroelectric properties are still unclear.

Research on possible applications of P(VDF-TrFE) in medicine or biotechnology was presented by Biggs *et al.*[116] For this purpose, mesenchymal stem cells were cultured on spin-coated P(VDF-TrFE) films for 7 days. Then, certain surface characteristics such as cell adhesion, topography, wettability, roughness and ferroelectric response were quantitatively assessed. It was found that the studied polymer was cytocompatible. Moreover, changing the polymer concentration makes it possible to regulate electrophysical film properties and cell adhesion.

In one of the recent studies, an innovative type of triblock copolymers, namely, poly(2-vinylpyridine)-*b*-poly(vinylidene fluoride-*co*-trifluoroethylene)-*b*-poly(2-vinylpyridine) [P2VP-*b*-P(VDF-TrFE)-*b*-P2VP] has been described. Different morphologies thereof (lamellar, cylindrical, and spherical) were obtained by controlling the ratio of blocks in macrochains. It was proved that at high P(VDF-TrFE) content, self-assembly of block copolymers proceeds. Morphology and crystallization within domains of copolymers have a significant impact on the ferroelectric response.[117]

6.3. Fluoropolymer laminates

The polymeric material is often used as a matrix for the piezoelectric or as one of the layers in an electronic device. Huiming *et al.*[118] developed an electret membrane representing a sandwich structure composed of three layers of perfluoropolymers: PTFE/THV/PTFE where THV is polymer containing tetrafluoroethylene (TFE), fluoroethylene-propylene (FEP) and vinylidene fluoride (VDF) units at a ratio of 45.8 : 18.5 : 35.7 (Fig. 5).[118]

The resulting multi-layer membranes demonstrated persistent and strong electrostatic effect due to synergy of three effects, namely, space charge injection, dipole orientation and interfacial polarization. The advantage of this system is its flexibility and resistance to elevated temperatures and environmental ageing. It has been concluded that an internal dipole charge within the middle layer is responsible for good performance of the electret membrane structure.

Recently, PVDF-based laminates with magnetoelectric (ME) properties have also been described.[119–122] The term 'magnetoelectric effect' means the properties associated with a reversible electrical response to a magnetic field. Studies of ME laminates lead to elimination of the disadvantages initially observed in such materials, *i.e.* insufficient coupling of component particles, brittleness, low stability, current losses, *etc.*

As was reported, ME effect can be achieved in PVDF laminates (piezoelectric) with metallic glass (magnetostrictive component), which contains iron and smaller amounts of other elements such as Co, Ni, Si and B.[121] Combination

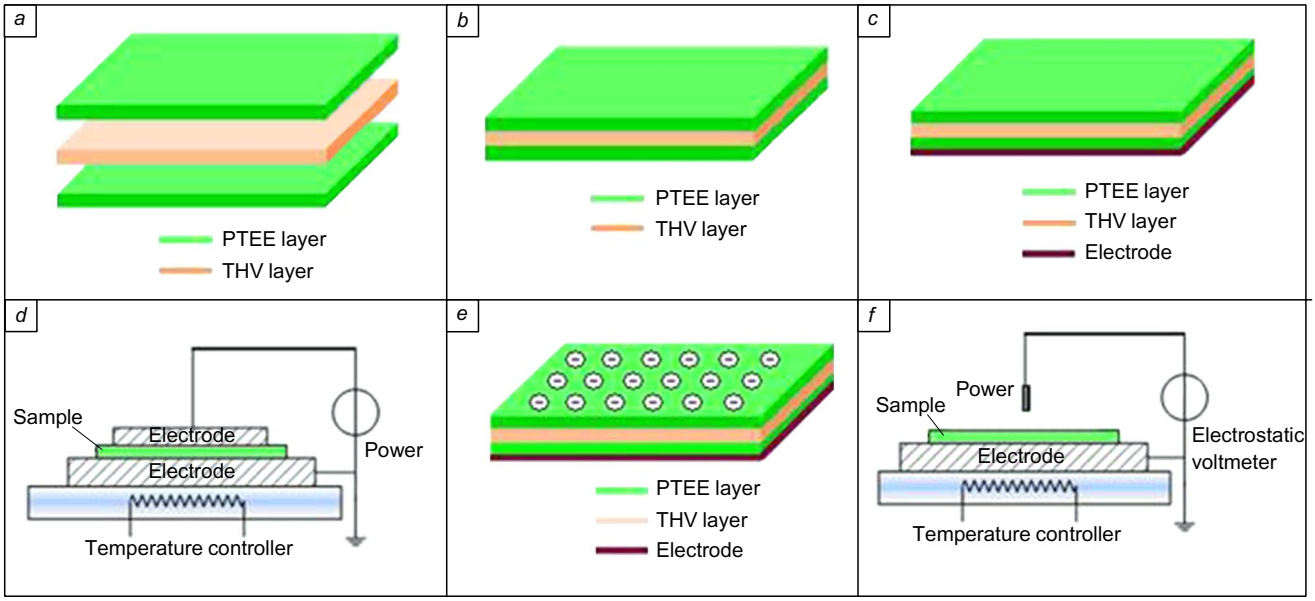


Figure 5. Illustration of a flexible PTFE/THV/PTFE electret membrane preparation.
Composition of a PTFE/THV/PTFE membrane (*a*); structure of hot pressed membrane (*b*), metallized membrane on the bottom surface with aluminium (*c*), schematic configuration of thermal charging (*d*), surface charge distribution of electret membrane (*e*), schematic configuration of surface potential measurement (*f*).[118]

of both components and formation of a heterostructure (*i.e.* laminated system) can induce high magnetoelectric voltage. The laminates obtained were composed of two or three layers. Such novel materials have potential application as sensors or actuators sensitive to magnetic field and energy harvesting devices. The original application proposal concerned the use of flexible magnetoelectric films as a device for collecting energy from power cables.[121]

6.4. Poly(vinylidene fluoride) nanocomposites

Piezoelectricity in polymers can be improved by incorporating inorganic piezoelectrics or carbon nanomaterials (described in Section 5) into their structure. Such systems form (nano)composites wherein the mechanical resistance, stiffness and thermal stability are enhanced, apart from piezoelectric properties.[77] In most PVDF-based composites, fillers are added for nucleation purposes providing appropriate crystallization required to impart the piezoelectric properties.

Examples of novel stretchable and flexible piezoelectric nanocomposites have been described by Park *et al.*[123] These were PVDF-perovskite hybrids that could be valuable materials for the generation of electricity, energy harvesting and self-powered energy system.

It has been reported that excellent piezoelectric material could be obtained by combination of organo-lead halide perovskite (specifically methylammonium lead iodide — $CH_3NH_3PbI_3$) and porous PVDF.[95] Such type of modification favours β-nucleation in PVDF, desirable for advantageous piezoelectric effect. The obtained system appeared to be photosensitive, which broadens its future applications in piezo-phototronic technology, for instance, as efficient photodetectors.

Environmentally friendly and durable composites were obtained from PVDF or its copolymer P(VDF-TrFE), used as a matrix, with a variable content of MgO nanoparticles of diameter < 50 nm.[124] Studies of their piezoelectric and ferroelectric properties showed significant improvement at 2 wt.% MgO: the piezoelectric coefficient increased by 50% and the voltage output was two times higher compared to a non-doped polymer. This effect was explained by optimal polymer chain conformation and its crystallinity degree as well as good nanoparticle dispersion. It was also suggested that additional factors favouring the improvement of piezoelectric properties included interactions between OH groups at MgO surface and macromolecules, which was confirmed by FTIR spectroscopy. In addition, the above nanocomposite exhibited high mechanical strength for multiple bending and resistance to electrical and mechanical fatigue.

Much attention is presently paid to nanocomposites based on of PVDF with allotropic forms of carbon with nanometric particle size.[125]

Such materials can be exemplified by nanofibres of graphene-reinforced PVDF obtained by electrospinning. In this case, a significant improvement in piezoelectric properties due to generation of β-polymorph was attained at a low content (0.1 wt.%) of graphene additive, contrary to the higher one. Complementary researches by DSC, FTIR and wide-angle X-ray scattering (WAXS) techniques have been performed, and the advantages of a nanogenerator based on this nanocomposite were demonstrated. Thus, providing a current capable of lighting a light-emitting diode (LED) lamp for 30 seconds under the force of a finger indicated the possibility to use this nanogenerator in self-charging personal devices.

The influence of the graphene addition on the microstructure as well as ferroelectric and piezoelectric properties of a PVDF film was investigated by Rahman and Chung.[126] A simple method to prepare this nanocomposite by a solution casting of PVDF and graphite oxide followed by a thermal reduction was presented. Significant improvement of desirable properties was observed at 0.3 wt.% content of reduced graphene oxide (RGO), suggesting the practical use of such nanocomposites as energy harvesters.

The multifunctional graphene – PVDF films designed for flexible diplays is another innovative idea.[127] This ultrathin sandwich structure exhibited three-dimensional touch interactivity: in $x-y$ plane due to graphene capacitive elements and in z-direction due to piezoelectric PVDF composite. By using different frequency bands both signals are detected simultaneously and three-dimensional touch sensing is achieved.

A flexible and transparent actuator/nanogenerator was prepared from a multilayer graphene/P(VDF – TrFE) film.[128] Proposed devices based on this system are characterized by a good efficiency and sensitivity in a broad range of frequencies. The output voltage obtained at the appropriate pressure was about 3 V and the current density was *ca.* 0.37 μA cm^{-2}, as comparable to the same characteristics obtained in mineral piezoelectrics.

Carbon nanotubes can serve as promising modifiers for piezopolymers.[129] Multi-walled carbon nanotubes in the amount of as low as 0.2 wt.% turned out to be a good nucleating agent for drawn PVDF, and at the same time, the rate of crystallization increased. Additional poling afforded the almost pure β-phase crystals.

Poly(vinylidene fluoride) based composites containing a mixture of NH_2-treated graphene nanodots (GNDs) and RGOs have been proposed for high energy density capacitors.[130] In this case, RGO induces formation of the β-phase in PVDF, while GNDs modified by ethylenediamine allow for hydrogen bonding with the polymer. Rather low content (10 vol.%) of combined fillers in a polymer matrix caused a significant increase of dielectric constant ($\varepsilon \approx 60.6$) and energy density [$U(e) \approx 14.1$ J cm^{-3}] compared to pristine PVDF [$\varepsilon \approx 11.6$, $U(e) \approx 1.8$ J cm^{-3}].

Self-powered nanocomposites suggested as novel energy harvesters were obtained by incorporating Fe-doped reduced graphene oxide into PVDF. In addition to piezoelectric properties, they showed electrical conductivity.[131] These nanocomposites were prepared by solution casting whereby mainly γ-phase of PVDF was formed. Films prepared from this composite did not require poling by electric field. Output voltage and short circuit current equal to 5.1 V and 0.254 μA, respectively, were obtained by repetitive human finger imparting. Electrical conductivity of composite containing as low as 2 wt.% filler was $\sim 3.30 \times 10^{-3}$ S cm^{-1}.

Another interesting material developed recently by Sinha *et al.*,[132] is PVDF modified by a graphene – silver nanocomposite (Fig. 6). Such modification provides an access to a new class of self-powered flexible plasmonic nanogenerators (PNG). A few graphene layers doped with Ag nanoparticles have been incorporated into PVDF. This resulted in an increased sensitivity to the visible light illumination (especially to that with the green light) and piezoelectric voltage changes leading to enhanced energy

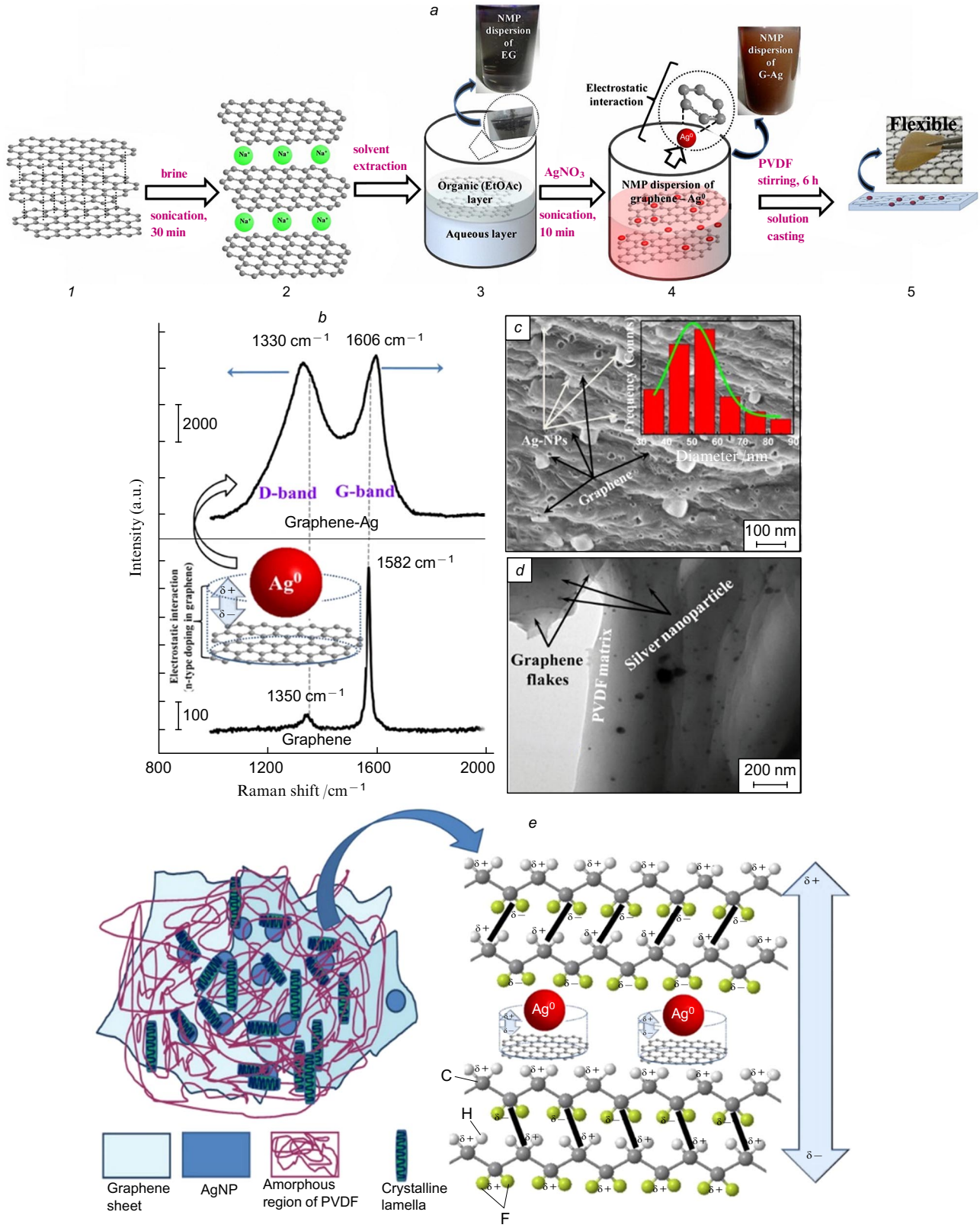


Figure 6. Schematic representation for (*1*) exfoliation of graphite through (*2*) the salt intercalation and preparation of (*3*) graphene, (*4*) graphene – silver (GAg), and (*5*) GAg-doped PVDF hybrid nanocomposite (PVGAg) (*a*). Raman spectra of GAg nanocomposite, downshift in G-band and upshift in D-band with respect to pristine graphene due to electrostatic interaction among Ag^o and graphene (shown in the inset) (*b*). Field emission scanning electron microscopy image of the PVGAg film with the histogram profile representing the diameter (~ 55 nm) of Ag-NPs (*c*). Transmission electron microscopy image of PVGAg film (*d*). Schematic representation of GAg induced self-polarization among the PVDF chains within PVGAg hybrid nano composite and the existence of GAg within the crystalline lamella of nucleated electroactive phase through this self-polarization (*e*).[132]

conversion efficiency (up to ~46.6%). Predicted applications include optoelectronic smart sensors and devices.

One more innovative and efficient piezo/triboelectric hybrid generator consists of two parts: arch-shaped PVDF (ferroelectric) layer placed between two Au films covered with polyimide (PI) and a bottom (piezoelectric) layer composed of Al-coated PTFE (wherein Al acts as a driving electrode for triboelectric generator).[133] The resulting device demonstrated high output voltage (~370 V), current density of ~12 μA cm^{-2} and power density of 4.44 mW cm^{-2}. The authors mentioned that the PI coating substantially increased the output voltage. The efficiency of such device can be illustrated by the fact that it lights 600 LED lamps just by finger pressing. Due to the relatively simple fabrication without the need to produce nanostructures, a low cost for such generators is anticipated.

Graphene/PVDF composite can also be applied as a binder in high performance MnO_2 supercapacitors. Using this composite in manufacturing of electrodes improves their electrochemical activity and stability, which can be attributed to chemical bonding between components. The best specific capacitance has been obtained with 5 wt.% graphene in PVDF.

Effective modification of PVDF to improve its dielectric properties has been achieved by application of novel conductive, carbonized PAN/PEG fibres. This type of fibrous filler was characterized by enhanced content of nitrogen and oxygen atoms at the surface, which led to increased interactions between fibres and PVDF. These interactions resulted in formation of ultrathin microcapacitors due to the possibility of intercalation of conductive fibres into dielectric polymer matrix. As a consequence, it was possible to obtain PVDF/fibre composite having the dielectric constant 150 times higher than that for pure PVDF.[134]

6.5. Polyolefins

Among a plurality of polymers with potential piezoelectricity, polyolefins constitute an important family. These compounds are characterized by a relatively low elastic modulus and sufficiently high crystallinity degree necessary for appearance of piezoelectric properties.[135] However, in fact, to obtain permanent electrets a special modification of the polyolefin structure should be performed.

As literature reports, various ways of modification are possible.[89, 90, 136 – 140] For example, polyethylene (PE) or polypropylene (PP) films can be oriented (uniaxially or biaxially), treated by corona discharge, subjected to post-processing treatment (under elevated temperature or pressure), foamed or filled with inorganic compounds as well as blended with other polymers.

Recently, we have demonstrated that the addition of a foaming agent to PE leads to formation of a cellular structure (Fig. 7), which ensures the accumulation of electric charges mainly at the interface of cavities.[141] A two-step method to obtain stable piezo-electrets from foamed PP has been developed (film extrusion and then its pressing at 140 °C). It was found that film compacted at elevated temperature has a positive effect on the polymer crystallinity, mechanical properties and piezoelectric constant. Stability of PP electrets was determined by thermally stimulated depolarization current. Calculated activation energy of depolarization process for extruded and additionally pressed films was 2.67 and 3.28 eV respectively.

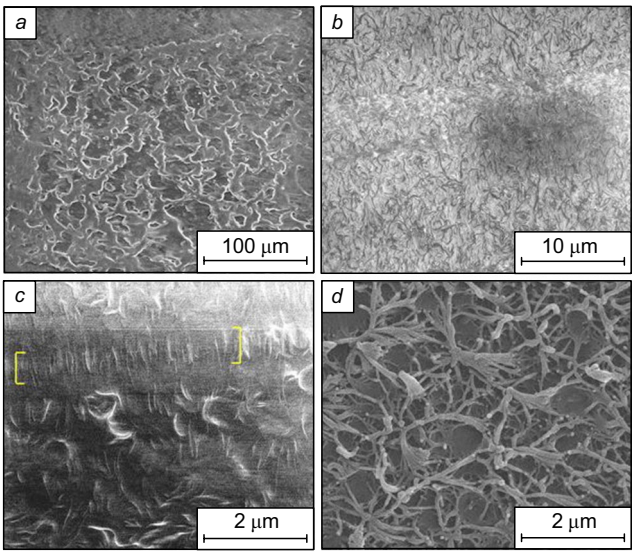


Figure 7. SEM images of blown, extruded medium density polyethylene film: surface of the gloss side (*a*), surface of the mat side (*b*), details on the mat side surface (yellow brackets indicate an ordered lamellar layer) (*c*), cross-section of the film after additional compacting at 140 °C (*d*).[141]

The cellular structure of polymers (referred also to as voided structure), particularly cell density, orientation, size and shape of voids is known to have a great influence on piezoelectric properties.[135] The proper, stable structure of this type can be obtained by carefully selected processing conditions and material composition. The application of two processes such as extrusion film blowing (or stretching) and foaming appeared to be a successfull solution to obtain the controlled 3D cellular morphology.

A detailed description of the cell structure formation, including individual stages and charging processes, models of such structures as well as mathematical formulas describing the piezoelectric effect can be found in the review by Hamdi *et al.*[135]

The cellular morphology in PE is also desirable for membrane applications, as described recently by Razzaz *et al.*[142] Here, porous hollow fibres from a combination of linear low-density PE with azocarbonamide as a blowing agent were obtained by extrusion. Moreover, it has been shown that optimization of manufacturing conditions (temperature, screw speed, feed rate, take-up ratio, blow-up ratio and the matrix composition) provided high cell density and uniform cell size distribution.

The same scientific group[135] also reported the optimization of the 3D cellular morphology of biaxially stretched thin PE foams produced by extrusion film blowing. In this case, talc as a nucleating agent was added to two types of PE [linear low-density PE (LLDPE) and low-density PE (LDPE)] along with the chemical blowing agent. Carefully selected conditions provided the formation of homogeneous and stable cellular structure from LLDPE/LDPE blend (with a weight ratio of 80/20). Moreover, this blend had an improved melt strength. The advantages of the obtained material suggest its potential application in piezoelelectric devices.

An effective method of modifying polyolefins to endow them with piezoelectric properties is doping with inorganic

silica-based modifiers such as kaolin or montmorillonite.[136, 138–141] For example, it has been found that the increase of silicate filler content in isotactic PP from 2.2 to 10% caused the rise of porosity and crystallinity degree (up to about 70%). This is reflected in enhancement of piezoelectric properties. Piezoelectric coefficient of i-PP composite (d_{33}) is in the range of 80–120 pC/N depending on the applied stress and this value is much higher than that in neat i-PP and even in PVDF chosen as a reference sample.[136]

Novikov and Smirnow[89] showed that electrets formed in polyolefins by high power X-ray radiation can be used for joining and polarization of two types of polymers (PE and PP) in cable insulation technology.

The US patent[90] describes porous electrets comprising a polymeric matrix (nonpolar PE with polar polymer having one or more functional groups such as an aldehyde, acid halide, anhydride, carboxylic, amine, amide, thiol, epoxide, alcohol, *etc.*) and ferroelectric additives, which can be one of a variety of inorganic or organic compounds (*e.g.* perovskites, tungsten bronzes, bismuth oxide thiourea and others).[90] Both components were initially blended to form a master batch, and then processed using a single- or multi-screw extruder. Ferroelectric substance can be incorporated into the polymer matrix by various methods (melt extrusion, solution or gel spinning, blown films). The obtained composites were designed for air filtration or dust removal. This invention was based on the assumption that the filtration efficiency can be enhanced not only by increasing the pressure but also by electrostatic charging of the filter material.

Another example of polyolefins with piezoelectric properties are elastomers built of ethylene–propylene–diene units (EPDM) and modified by multi-walled carbon nanotubes (MWCNTs).[143] Mixing the components in solution enabled good dispersion of conductive MWCNTs in form of comminuted agglomerates in an insulating polymer matrix. Composites containing 0.5 wt.%–5 wt.% MWCNTs had better mechanical properties than non-filled EPDM. Repeating loading experiment demonstrated that conductivity consists of irreversible and reversible part (which was attributed to piezoresistivity). The electrical behaviour, particularly the relationship between resistivity and mechanical deformation, suggests their possible application as a new generation of strain or pressure sensors.

A piezoelectric material was obtained from PP filled with $CaCO_3$ microparticles of different size (3–12 μm) and concentration (3 wt.%–44 wt.%).[144] Formed composite had a cellular structure, which was then expanded *via* biaxial stretching and gas diffusion expansion. It was found that preferred voided structure was formed in the PP film containing >23 wt.% chalk with a particle size of 12 μm. Furthermore, it was estimated that the average cell size (5–8 μm) in this system is beneficial for corona discharge treatment in order to obtain stable piezo-electrets.

6.6. Other piezoelectric polymers

It has been recently reported that the main factor influencing the piezo/ferroelectricity of polyamides (nylons) is the presence of mesophases with enlarged interchain spacing and distorted hydrogen bonds.[145] Here, it was shown that not only the odd nylons can be characterized by piezoelectric properties, as was previously thought, but also even polyamides with defected structures. These achievements formed the basis for design of proper crystalline structure of this class of polymers with enhanced electroactivity.

An effective energy harvesting system based on polyurea thin films, subjected to vibrations, has been proposed.[91] The polymer was obtained *via* vapour deposition polymerization with 4,4′-diphenylmethane diisocyanate and 4,4′-diaminodiphenyl ether. The device was built from polyurea film attached to a beryllium copper cantilever. Vertical vibrations were applied and the output voltage was measured. Numerically calculated perfomance of conversion energy indicated that the system effectiveness depends on cantilever configuration, which has been confirmed by experimental results. The best efficiency was obtained using a thinner and shorter cantilever and increased resonance frequency.

Polymer electrets based on thiophene and selenophene donor–acceptor polyimides have also been characterized.[146] It was found that such types of polymeric electrets have an improved ability to transfer and store the electric charges, thus their application as novel organic transistor memory devices seems quite real in the near future. Particularly favourable properties were observed in a polymer with strong electron-rich selenophene moieties, which showed the highest field-effect mobility of electrons and the largest memory window among the studied systems.

Magnetoactive electrets (not synonymous with magnetoelectrics) are innovative materials combining both piezoelectric/ferroelectric and magnetic properties.[96, 147, 148] Such materials can be obtained by incorporating carbonyl iron particles (used in magnetorheological fluids[147]) into elastomer matrix able to form electrets *e.g.*, to polydimethylsiloxane (PDMS). An additional modification of polymer with highly electrically polarizable particles of $BaTiO_3$ increases the trapped charge. The application of other magnetic particles such as permendur (a cobalt–iron alloy) or neodymium magnet (NdFeB) has also been suggested.[148] The desired material was obtained using a modified 3D printing technique (through extrusion or injection), layer by layer, named 6D printing. Thus a perfect material without defects can be prepared. The devices built of magnetoactive polymers (MAPs) containing electrets exhibit interesting properties, *e.g.*, permanent magnetism and simultaneous electrostatic polarization as well as possibility to operate under both electric and magnetic fields. The integration of MAPs and electrets leads to mechanically flexible actuators, which are promising elements for robotic technologies.

A method to obtain highly active piezoelectric composites of PDMS with lead zirconate titanate (PZT) by freeze-casting method has been developed.[149] This technique leads to the formation of a specific porous structure on ice template. A characteristic feature of this structure is the presence of unidirectional channels (*i.e.* pores being a replica of the ice crystals), responsible for high effective longitudinal piezoelectric coefficient. Such structure is responsible for enhanced piezoelectric properties and high flexibility (possibility of bending to a small radius), low cost and easy fabrication in any shape, and represents a promising material for broad application as self-powdered sensors of pressure and shear.

Micro-structured cellular PDMS was obtained by moulding process and then poled under specified conditions.[150] Properties of PDMS depended on the charging temperature. After poling at room temperature, piezoelectric coefficient was very high (d_{33} = 350 pC/N; *ca.* ten times higher than that for PVDF) and the elastic modulus was low (300 kPa).

When charging at higher temperature, the piezoelectric properties were a bit worse but thermal stability was improved. The application for wearable device production was suggested.

Polymethyldisiloxane was also used to design a flexible capacitive microsensor for measuring the foot pressure during walking.[151] By varying the content of the curing agent, the material stiffness can be controlled. The composition with a 16 : 1 ratio of prepolymer : hardener was selected for simultaneous analysis of the normal and shear forces since in this case a linear stress – strain relationship was found.

Crosslinked polystyrene containing ionic groups in backbone and mobile counterions in non-equilibrium quantities is an example of ionic electrets — materials capable of bearing a long-lived electrostatic charge.[20]

Charged microspheres (50 – 450 μm diameter) were obtained from polystyrene based-ionomers through contact electrification. As ionic groups covalently bound to the polymer, tetraalkylammonium, alkyltriphenylphosphonium, sulfonate or sulfonated azobenzene functionalities were used. The content of introduced groups was very low (5% – 10%). Counterions can be transferred to another substance upon direct contact or even through a gaseous barrier. The schematic illustration of the ion-transfer mechanism of contact electrification is presented in Fig. 8. The factors influencing this process (type of ionic groups, various gas atmosphere and humidity) have been studied. It was shown that the charge on microspheres was proportional to the surface area. Moreover, the dielectric breakdown of the gas medium limits the charge accumulated on electrets. The sign of charge on a sample can be predicted and adsorbed water or hydrophilicity of the material causes dissipation of charge. Inorganic materials (glass, silicon) can be also functionalized with ions leading to ionic electrets, which can exhibit similar charge transfer from one to another surface upon contact. It was possible to obtain charge patterns on planar silicon surfaces and on glass microspheres. This method can serve to prepare electrets with reproducible properties for application in laser printing or photocopying processes. The clarification of electrization mechanism is also useful so as to prevent undesired charging of materials.

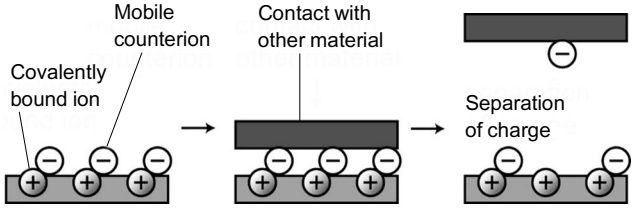
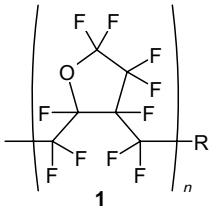


Figure 8. Schematic illustration of the ion-transfer mechanism of contact electrification.[20]

Some works focus on detailed studies of end groups in perfluorinated polymers on electron trapping.[152 – 154] It has been found that the surface charge density is increased by introduction of functional end groups such as trifluoromethyl, carboxyl or amidosilyl to cyclic transparent optical polymer (CYTOP).[154]

Structure 1



1

R = CF_3, CO_2H, $C(O)NHC_3H_6Si(OEt)_3$

Moreover, the charge stability and thermal resistance can be significantly improved by this modification. A particularly beneficial effect was observed in perfluorinated heterocyclic polymer **1** functionalized with amidosilyl end groups.[153] The higher surface charge density was also noted for carboxyl-ended CYTOP, additionally modified by aminosilane derivatives. The resulting structure, confirmed by SAXS, AFM and SEM techniques, consisted of organic siloxane nanoclusters (with a diameter of ≈20 nm) embedded in a polymer matrix. These nanoclusters act as charge traps.[152] An additional advantage of perfluorinated polymers is their solubility in fluorinated solvents, which makes it possible to use the spin coating method to obtain electret films. The experimental results are in good agreement with quantum mechanical calculations by the DFT method, adopted to determine the orbital energies and electron affinities of CYTOP.[154] The conducted research allowed estimating the suitability of this material for production of micro-power generation devices.

Polyimide (PI) containing polar functional groups also exhibits piezoelectric effect. Besides exceptional mechanical and dielectric properties, PIs are characterized by high thermal resistance (up to 400 °C). Therefore, PI-based sensors can be used at high temperatures (even at 150 °C) where PVDF is eliminated. Research on the use of PI was carried out at NASA by Atkinson *et al.*[155] The mesoscopic scale tactile sensors built of cantilever and bridge structures with upper and lower electrodes and an integral self-test electrode have been developed. Bridge sensors were obtained by a multistep procedure.[156] The lithography and metallization method was used to prepare the support electrodes and then, polyimide film was spin-cast onto the wafer (a thin slice of semiconductor). Chemical modification of PI resulted in a lower curing temperature below 125 °C.[156]

Flexible transducers on polyimide substrates were developed by Petroni *et al.*[157] The authors described the manufacturing protocol of microelectromechanical systems (MEMS) composed of molybdenum electrodes (top and bottom) and the aluminium nitride active layer deposited on a polymeric tape (PI with silicone adhesive). Such devices can find application in robotic systems and prosthetics.

Another group of piezoelectric materials presents parylenes based on poly(*p*-xylylene), prepared mainly by chemical vapour deposition polymerization (CVD).[158, 159] Here, the poling conditions are of special importance. Charging at electric field of up to 40 MV m^{-1} and high temperature (250 °C) provides high values of piezoelectric coefficient (d_{33}).

New possibilities of parylene manufacturing are provided by plasma deposition polymerization.[160] In this type of polymerization process, the solid precursor undergoes cracking and sublimation upon plasma action (*i.e.* during

collisions with electrons and UV photons). In this way, pyrolytic decomposition of a substrate occurring under typical CVD conditions is omitted. Advantages of plasma polymerization comprise high rate as well as the possibility to control morphology and properties of the resulting parylene films (by controling the plasma conditions).

An innovative proposal to production of piezoelectric nanogenerators on the base of hybrid materials has been reported by Lee *et al.*[161] Reinforced composites were obtained by dispersion of amine-functionalized lead zirconate titanate nanoparticles in a thermoplastic triblock copolymer grafted with maleic anhydride. This material combines good piezoelectric properties (output voltage of 65 V and current of 1.6 μA), durability and high flexibility typical of polymers.

Poly(L-lactic acid) (PLLA), which is a known biodegradable polymer, also exhibits piezoelectric properties. This substance has been recently suggested as a material to produce wearable piezoelectric fabrics, sensitive to human motion, including bending and twisting. Such smart (or intelligent) clothes can be used to convert energy from human movement into electricity.[162–164]

7. Piezoelectric biopolymers

Research on the phenomenon of piezoelectricity in natural biological materials, initially in wood, then in proteins (*e.g.* from bones), has been performed as far back as the 1950s by Fukada and Yasuda.[165, 166] Also, natural waxes and resins are often cited as the earliest known piezoelectric substances.[6–8, 10]

Piezoelectric properties of proteins arise from the internal rotation of the dipole moments of C(O)NH groups bonded to the asymmetric carbon atom and formation of strong intermolecular C—H bonds among the polypeptide chains. Among this group of substances, piezolelectric properties have been observed in biopolymers containing both L- and D-amino acid isomers but not in DL-forms. Piezoelectric polarization of these structures is most probably associated with the rotation of dipole polypeptides forced by extraneous stress. It was also found that the piezoelectric properties strongly depend on the water content. The studies of piezoelectricity in biopolymers have mostly been focused on collagen (with its characteristic structure of a triple helix), which is a natural protein of bones, tendons, cartillage, ligaments and skin. The bio-piezoelectric effect of ordered native collagen was confirmed in 1957 and 1964 by investigations of Fukada and Yasuda,[165, 166] who found the correlation between higher crystallinity and biopolymer order (polar hexagonal structure of the collagen unit) and its piezoelectricity. These results have also been observed and confirmed by other researchers.[167, 168]

Nowadays, the reliable method that perfectly confirms the piezoelectricity of single collagen fibrils is piezoforce microscopy (PFM), which has been successfully used to study bio-nanomaterials. This method reveales polarization of fibrils along their axis and lateral piezoresponse. Contribution of simultaneously observed vertical radial piezoelectric effect was negligible.[81, 169, 170]

Furthermore, it was observed that the crystalline structure of collagen depends on ambient conditions. As previously mentioned, the bound water has a significant influence on crystal symmetry in collagen and can lead to the point where piezoelectric properties disappear. Differences in electroactive behaviour of collagen under wet and dry conditions directly affect the piezoelectric properties of the bones.[81]

Type II collagen dominating in bones and articular cartilages plays a significant role in regulating some stress-induced processes and regeneration of the damaged tissues. It is very likely that piezoelectric properties of collagen will be useful in treating many diseases that today are a significant problem (*e.g.*, osteoporosis, osteoarthritis, osteopenia, articular cartilage damage due to trauma or mechanical overload, *etc.*). Collagen in combination with other components can be used to obtain smart biocompatible, three dimensional, piezoelectric scaffold with a potential application in fast tissue regeneration. Initially, such scaffold is subjected to a controlled damage with some external loads in order to convert the functional stress into electrical signals by the piezoelectric phenomenon. The controlled electrical stimuli can promote a cell proliferation leading to synthesis of tissue material.[171]

It was reported that piezoelectric collagen fibers are able to promote the growth of chondrocytes upon the cartilage regeneration. The voltage-gated calcium channel of chondrocytes is activated with electrical stimulation, which consequently promotes the influx of extracellular calcium ions. Then, calmodulin and calcineurin are activated. The next step is dephosphorylation of a nuclear factor and the expression of genes responsible for cell growth during the cartilage regeneration.[171]

The latest researches have also been focused on applications of bio-waste eggshell membranes (EGM), which are valuable source of collagen. They exhibit good piezoelectric properties: high piezoelectric coefficient ($d_{33} \approx 23.7$ pC/N), output voltage ~26.4 V and current ~1.45 μA. The energy conversion is also high (63%). Furthermore, such natural membranes are porous, biocompatible, biodegradable and cheap, and the production of bio-nanogenerators based thereon has been proposed. Connection of five small generators of such type affords an efficient piezoelectric device capable of switching on more than 90 LEDs. It should be added that such device is characterized by very high sensitivity. The generation of current occurs under the influence of small forces, *e.g.* is arterial pulse, cough or body movement.[172]

It has been reported that onions represent one more source of novel piezoelectric biomaterial.[173] Similarly to EGM, this raw material is characterized by biodegradability and biocompatibility. It was proved, that an untreated onion skin, as a fibrous cellulose bioproduct, is an efficient piezoelectric generating high output voltage and current with the piezoelectric coefficient of ~2.8 pC/N. It is expected that such materials will find medical application, *i.e.* in cardiac pacemakers, where they will be responsible for generating biomechanical energy.

Some other biopolymers also possess piezoelectric capacities resulting from their non-centrosymmetric structure. They include polysaccharides [cellulose (wood, ramie)], chitin (crab shell, lobster apodeme, wings of butterflies, cell walls of fungi); amylose (starch); proteins (silk fibres); collagen (bone, skin tendon), and even viruses; keratin (wool, horn) as well as fibrin (elongated films of fibrinogen-thrombin clot, deoxyribonucleic acids). However, these biomaterials have relatively low values of d_{14} coefficients (0.1–2 pC/N) — generally up to 20 times smaller than that of the quartz crystal.[81]

Piezoelectricity effect of α-keratine (the main constituent of mammalian hair, wool and horn) has been found as far back as in 1940 by Masuda.[174] Recently, it was reported that determining the dielectric properties of keratin contained in human nails could be useful in detection of some diseases, such as diabetes.[175] Different properties of keratin from healthy and sick people were shown to depend on changes in its chemical structure resulting from destruction of hydrogen bonds and polar keratin chains in humans suffering for diabetes. Moreover, the differences in activation energy of β-relaxation in kerain from the diabetic person compared to the healthy one suggest that glycation end products may form cross-links.[175]

A novel class of piezoelectric peptide-based nanomaterials includes diphenylalanine nanotubes, which are self-assembled, functional and chemically stable.[176] The determined piezoelectric constants of diphenylalanine were: d_{33} = 18 pC/N and d_{31} = 4 pC/N.

Currently, very promising results have been obtained in the studies on piezoelectricity of chitin both in its pristine form or as its deacetylated derivative, *i.e.* chitosan.[177–179] Chitin, which is a polysaccharide composed of β-(1→4) linked N-acetylglucosamine monomers, exists in three crystalline forms: α, β and γ. The first form (α-chitin), found among others in crab shells and butterfly wings, exhibits piezoelectric properties. Its intrinsic molecular polarization due to the non-centrosymmetric crystal structure, high optical transparency and bending characteristics make chitin a promising electronic substrate.

Arrangement of chitin macromolecules can be improved through the electrospinning process, which includes shear and elongation forces, and consequently makes it possible to control the degree of crystallinity of the produced nanofibres. Furthermore, chitin piezoelectricity and crystallinity can be controlled by varying electrospinning collector type — application of the air gap collector ensures the better properties than the flat plate collector.[177]

Electrospun chitin forms nanofibres with a core–shell structure (highly piezoelectric exterior and a less active interior), which can find application as an effective heavy metal filter for drinking water.[177] Despite many beneficial properties there are some disadvantages limiting its practical application such as poor processability because of low thermoplasticity and low solubility in most organic solvents.

Biodegradable piezoelectric device based on a transparent film made of crystalline chitin nanofibres has been designed and thoroughly studied by Kim *et al.*[180] The piezoelectric transducer was fabricated on the base of solubilized and purified β-chitin obtained from squid pen extract in a form of flexible nanofibre film by a centrifugal casting processes. It should be mentioned that the resulting piezoelectric chitin film turned out to be fully biodegradable by a chitinase enzyme within eight days without any toxic residues remained.

Piezoelectric properties of chitin derivative — chitosan — also result from its non-centrosymmetrical structure. Dissolving chitosan in formic acid (compared to other acids, *i.e.* acetic, adipic, and succinic) gave flexible, user-friendly and more stable films which could be used as an element for vibration sensing. The d_{33} coefficient, determined under various pressures, was maximal (18.4 pC N^{-1}) for a load of 5 tons. High thermal stability of the sample (up to 330 K) has been confirmed. Further temperature increase led to a decrease in the d_{33} coefficient, which may be due to the disappearance of non-centrosymmetry of chitosan. Furthermore, very high isolation resistance (from 0.4 to more than 1 GΩ) enables its application in vibration or mechanical sensor elements.[178]

Natural wood cellulose is characterized by some interesting properties. Fibres of this substance are oriented towards the axis of the tree trunk, so the wood can be treated as a system of monoaxially oriented cellulose crystallites determining the piezoelectric properties of wood. Replacement of cellulose hydroxyl groups with acetate ones, as well as water absorption, leads to changes in piezoelectric and dielectric properties. Since the piezoelectric coefficient of wood cellulose is very low (d_{14} = 0.1 pC/N), its applicability as a material for piezoelectric sensors is rather problematic. However, the piezoelectric effect turned out to be more pronounced in cellulose nanocrystals (CNC), which are characterized by a very high permanent dipole moment.[181] It was found that orientation of CNCs has a significant influence on the piezoelectric response (Fig. 9).[182] Moreover, comparing CNCs to cellulose nanofibrils (CNF) containing both crystalline and amorphous phases, the latter material seems to be more versatile and has a wider range of applications. Nevertheless, there are still only few scientific reports devoted to this subject.[176, 181, 183]

Very promising materials for sensor and actuator applications are films based on mixed chitosan and cellulose, however, the final piezoelectric properties depend on the chosen combination of polymers and their forms (nanofibrills or nanocrystals).[184] It is also worth noting that blending chitosan with nanocellulose affords 'green' piezoelectric materials with enhanced durability. Modification of the molecular alignment, and thus piezoelectric properties, can be achieved by action of electric field on polymer film.[185]

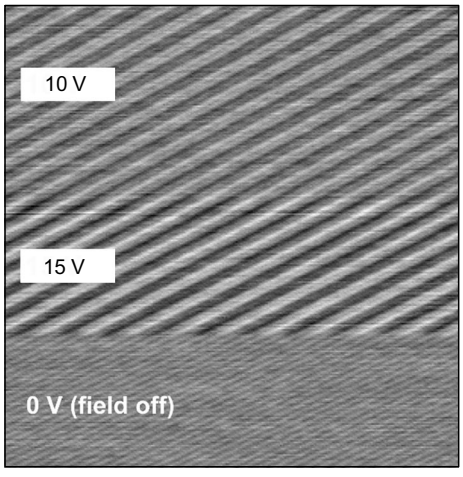


Figure 9. Map showing the extent of cellulose nanocrystal film displacement (*z* direction) as a result of its piezoelectric effect. The extent of displacement is indicated by lighter or darker fields as monitored by an atomic force microscopy (conductive) diamond tip in contact with the film. A single point was monitored under given intermittent electric fields (10, 15, and 0 V). The deflection measured was used to calculate the piezoelectric constant of the films. The *x* and *z* scales in the image are dimensionless but indicate film deflection evolution with time as the voltage is turned on and off.[182]

Cellulose-based composite with ZnO nano-layer (ZONCE) also seems to be a very promising piezoelectric material.[186] Such a system was designed to increase its piezoelectric charge constant. The final composite properties were greatly influenced by the fabrication method in use (nanocoating, blending or ZNnO nanorod growth on a cellulose blend). More satisfactory results were obtained by the method wherein ZnO was growing on cellulose films rather than on cellulose pulp or fibrous paper since in the former case both piezoelectric and mechanical properties as well as transparency of films were more suitable. Furthermore, it was noticed that certain parameters such as dielectric constant, dielectric loss factor, and piezoelectric charge constant depended on the interfacial polarization (associated with the preparation time). To improve piezoelectric properties of the samples, twice-hydrothermal process was conducted as providing more precise nanocoating of the cellulose surface with ZnO. Also, a significant increase in d_{33} value was observed compared to the pure cellulose (23.4 and 3.40 pC/N respectively).

Recently, the possibility of using viruses (more specifically, virial proteins — M13 bacteriophage) for fabrication of piezoelectric energy generator has been reported.[187, 188] Here, the generated current is enough to operate a liquid crystal displays. Thorough virus observations have demonstrated the twisting of protein helices and their ability to self-organize under the influence of external stimuli. The genetic engineering leading to introduction of charged amino acids into protein structure and twenty-layered arrangement significantly improve the piezoelectric effect. Due to a very rapid growth under appropriate conditions, viruses can be considered an inexhaustible source of valuable biomaterial.

8. Methods of characterization of piezoelectric materials

In the design of piezoelectric materials and in order to explain the structure – property relationship, it is necessary to determine their physicochemical characteristics. For this purpose, standard instrumental techniques such as absorption spectroscopy (FTIR, UV-Vis), X-ray diffraction analysis (XRD), thermal analysis (DSC, DTA), scanning microscopy (SEM, TEM, AFM) and mechanical tests are usually applied.

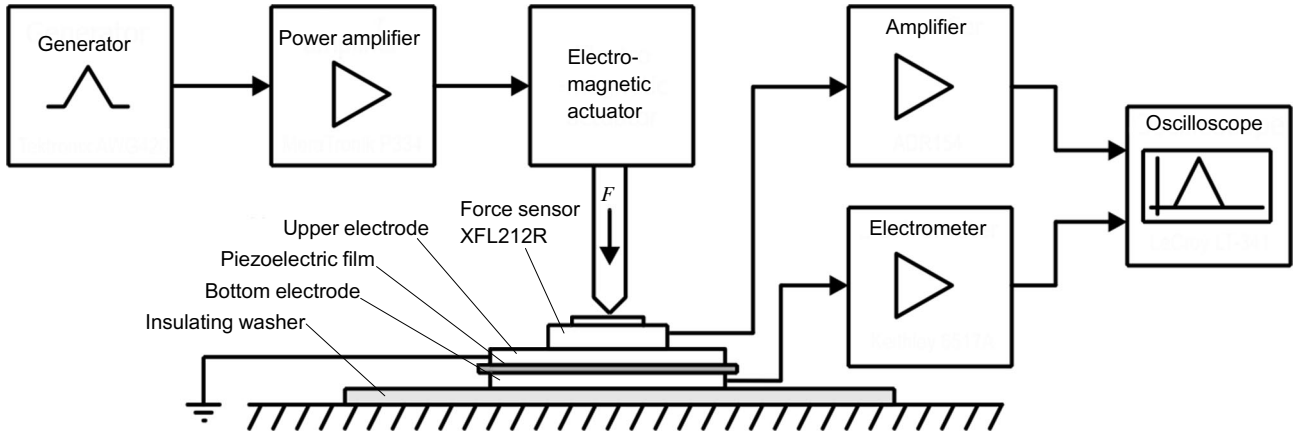


Figure 10. Diagram of the compression test stand.[138]

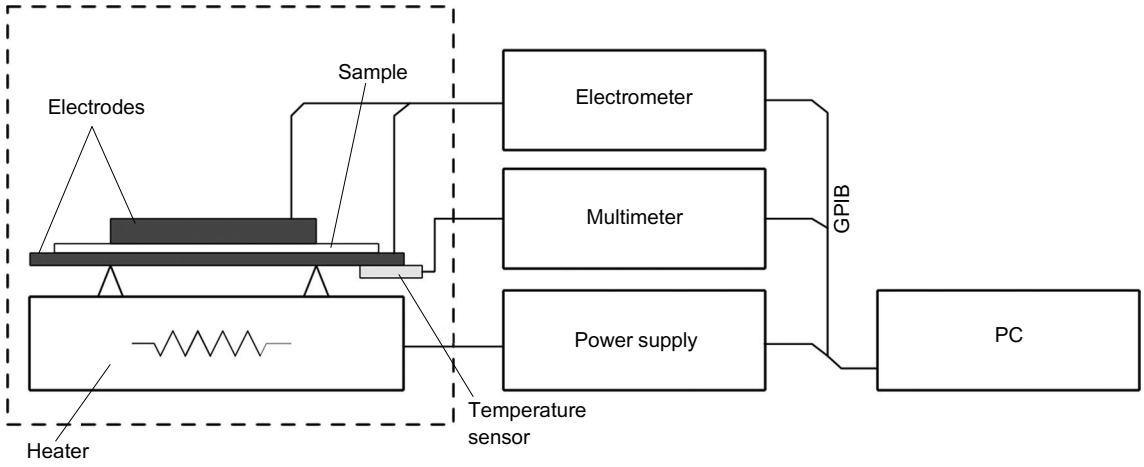


Figure 11. Diagram of thermally stimulated depolarized current measuring system.

To investigate piezoelectric properties in a polarized material, the charge density (q) and the voltage (U) of current generated under an applied stress are measured.[1, 3–5, 7–9, 37] The diagram of the measuring setup is illustrated in Fig. 10.

The sample in the form of a thin film is placed between two conductive electrodes. The good contact of the sample with the electrodes is important for correct measurements. Alternatively, a layer of silver or gold metal can be applied to the test sample (it may be a metal paint or a vapour deposition).[17]

To check the durability of the piezoelectric effect necessary for practical applications, a long-term monitoring of the above-mentioned parameters is required (sometimes within few months).

Also, the thermally stimulated depolarized current (TSDC) method is useful to study piezoelectrets, allowing detection of the relaxation processes at elevated temperatures. Using the TDSC method, one can determine the temperature upper limit below which the electric properties are unchangeable, *i.e.* the temperature range wherein a given piezoelectret can be practically applied. This method is based on measuring the discharging current depending on the temperature (Fig. 11).

At room temperature dielectrics show no electrical effect. As the temperature increases, the discharge current appears, reaching its maximum value at a temperature specific for a given material. From a practical point of view, the temperature of the onset of changes in the current density (J) is an important parameter. Plotting the logarithmic dependence of current density from the reciprocal temperature ($1/T$) can serve to calculate the approximate activation energy of depolarization. Then, one can calculate a straight line curve fit for subsets of the starting points of the designated range using the least squares method and the best correlation coefficients. The slope of line can be applied to calculate the activation energy of depolarization according to Arrhenius equation.

Piezoelectric materials, including polymers, exhibit nonlinear displacement as a function of an electric field (E), which is observed as a hysteresis loop (Fig. 12).[189, 190] Applying electric field to piezoelectric element, the polarization maximum is achieved. Lowering E to zero allows one to determine remanent polarization (this is the value corresponding to the intersection of the ordinate axis).

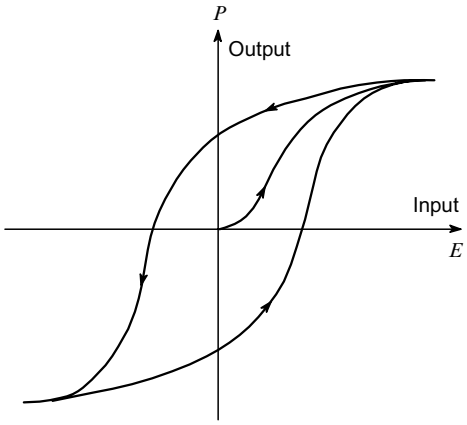


Figure 12. Hysteresis loop of piezoelectric materials representing a memory-like effect, where the output is independent of the input.[189]

A method of testing piezoelectric surfaces is Kelvin probe force microscopy (KPFM).[191] This method implies simultaneous imaging of surface potential difference and topography, thus, it is a useful tool in studying electric properties of materials.[192] The silica was locally charged by conductive AFM applying a conductive tip (Ti-Pt). It was found that charges were stored in particular traps. Moreover, charge dissipation, depending on hydrophilicity/hydrophobicity of the surface, is realized in two ways (parallel or perpendicular to a substrate). Hydrophobic coating of a specimen stabilizes the stored charges. In this study, the possibility of selective and controlled attachment of dye (Rhodamine 6G) to negatively charged centres in modified SiO_2 has been demonstrated and confirmed for the first time by confocal microscopy.

An example of application of AFM (both classic one and KPFM) in studies of SiO_2 electrets was reported by Zhang *et al.* (Fig. 13).[193] In this work, AFM tips were modified by treatment with air plasma or piranha solution (sulfuric acid + H_2O_2). Moreover, the tip surface was functionalized with 3-aminopropyldimethylethoxysilane to

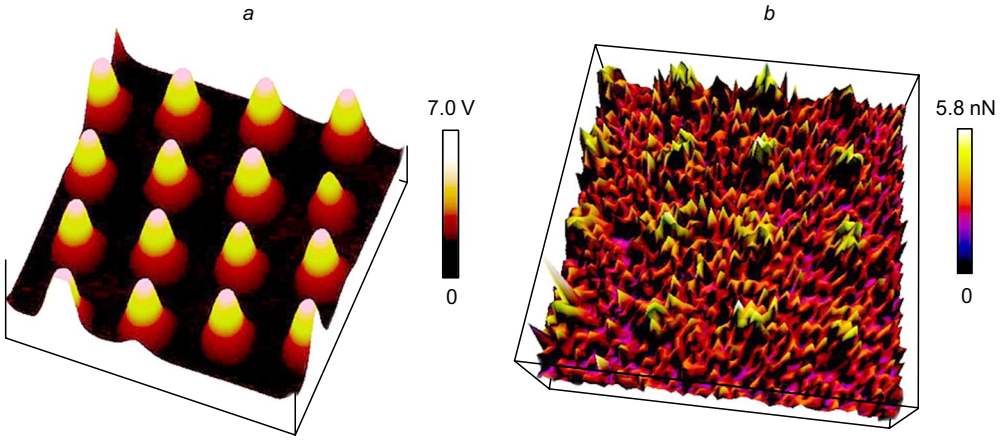


Figure 13. Electret characterizations: 3D Kelvin probe force microscopy (KPFM) image (*a*), 3D force map using a plasma-treated atomic force microscopy (AFM) tip (*b*). The image sizes are 30×30 μm.[193]

modify the interaction between the AFM tip and SiO_2 surface. The tip–silica adhesion has been calculated from the force-displacement curves. Also, the information on modulus, deformation and energy dissipation was achieved. The authors demonstrated that AFM enables mapping of electrostatic charges deposited on SiO_2, which extends the possibilities of testing electrets, because, as was previously mentioned, KPFM requires application of conductive probes.

9. Application of contemporary piezoelectric materials — selected examples

The use of piezoelectric materials in everyday life and the economy is still expanding. Some of their applications have already been mentioned in the previous Sections. The rapid development of scientific studies of novel piezoelectrics is based on the expectations of consumers who want to use comfortable, personal and portable electronic devices, becoming ever cheaper, smaller and more reliable.

In addition to typical piezoelectric applications (such as actuators, ultrasound or light generators, transducers, sensors, sounders, crystal watches, micromachines, elements of SPM and ink jet printers), more and more new ideas can be found in the current literature.[12,75–80,84] A few of them are shown below.

Of particularly great interest is the possibility of energy harvesting using forces from various sources (*e.g.* energy of wind, rivers or human legs during walking).[77,80,194,195] The idea of using piezoelectric materials as energy harvesters lies in the quest to obtain energy from the environment that is often unnecessarily lost. Thus, the conversion and storage of such dissipated energy is extremely important for economy and ecology. Composites based on PVDF have a fatigue resistance and good stability against environmental factors, however, energy obtained therefrom is rather low (in the microwatt range).[80] Therefore, further intensive research is currently in progress to improve the material properties and upgrade the already constructed devices.

Advances in piezoelectric material technology allow their use in obtaining energy from street traffic or highway. Both types of piezoelectrics based on polymers and ceramics are suitable as road energy harvesters.[196–199] The proper piezoelectric module design can result in getting a big power output of PVDF. For example, application of strain amplifying module with a particular bridge-shaped geometry amplifies 2.5 mm vertical displacement to 13 mm horizontal one.[197]

The obtained power density was 16.5 W m^{-2} at a car speed of 80 km h^{-1}. Moreover, the final effect depends on the car speed, thus besides energy harvester, such device can be used as self-powdered speed sensor.[197] Some technological solutions have been tested under real road conditions.[198,199]

In literature, one can find information about the application of piezoelectric materials in new techniques of scanning microscopy and spectroscopy allowing for nanoscale characterization of materials.[200,201] The use of piezoelectrics in AFM enables imaging of the complex structure of ferroelectric and piezoelectric domains with high spatial resolution as well as explanation of their intrinsic properties.[201] Furthermore, quantitative piezoelectric measurements can be done by piezoresponse force microscopy (PFM) and piezoelectric coefficient can be precisely determined by recording the current produced by piezo-materials as a result of the force action.

It was shown that PFM is also a useful technique for studying of electrical phenomena in non-piezoelectric substances and polarization switching properties of ferroelectrics.[202]

In addition to conventional applications of piezoelectric materials, the number of those converting the work performed by living organisms, including humans, into electricity, which can be stored and used for everyday devices, is increasingly growing.

Electroactive macromolecular compounds are valuable materials to prepare artificial muscles that can be used in robotics or medicine (*e.g.* in surgery as smart prostheses and tactile sensors) and even in toys.[203–205] The great challenge is to develop an artificial structure imitating the structure of natural muscles. Among their benefits, high fracture tolerance, large actuation strain, high toughness, vibration damping can be mentioned, in addition to other advantages typical of polymers.[203] The problem to be solved is limited actuation capability and low energy density, insufficient for practical applications.

Apart from conductive polymers, piezoelectric (dielectric) ones imitating the muscle action are good candidates for the above-mentioned applications. Some artificial muscle technologies use materials which are characterized by a response to heat or light.

Another type of synthetic muscles are ionic electroactive polymers including ionic polymer–metal composites (IMPC).[204] The polymeric component is a polyelectrolyte, coated with two metal electrodes. Applying voltage to thus formed trilayered actuator causes its bending with a consequent moving of solvated mobile ions. The structure of ionic polymer is typical of ionomers, in whose clusters ions are surrounded by hydrophobic polymeric backbones.

An interesting application of IMPC is an artificial protective coating imitating natural skin. Interestingly, one may use electroactive elements from IMPC to remove the dust from window surfaces.[203]

Among dielectric elastomers that provide high strain, silicones or acrylic polymers can be distinguished. They are sometimes modified by titanium dioxide in order to increase their dielectric constants.[204] The actuator is built by placing an elastomer between two electrodes (made up from graphite, silver paste or other conductive material). It is possible to increase the performance of equipment based on these elastomers due to their special architecture (stacking in layers as well as rolling into tubes).

Electrostrictive ferroelectric polymers (*e.g.*, PVDF copolymers) and liquid crystal elastomers (based on siloxanes with diphenyl type mezogenes) are other examples of materials suitable for artificial muscles.[204]

The very important role of piezoelectrics in terms of their medical, dental and pharmaceutical applications cannot be omitted.[206–210] They can serve as sensors of various types used in diagnostics (*e.g.*, small and flexible blood pressure gauge, respiration rate sensor), ultrasound scanner for medical imaging (*e.g.*, allowing observation of the embryo in the mother's womb), ultrasonic surgery instruments (allowing for a precise and not invasive surgical treatment), piezoelectric ultrasonic scalers for removing plaque and calculus from teeth or dental implants.[210] Particularly, miniaturized arterial pressure sensors that can be mounted on the skin of the wrist are very comfortable in

use and allow self-control of health and a quick help when needed.[206]

Ultrasonic image is created basing on the echo time of the ultrasound and Doppler shifts of the reflected sound. The ultrasonic waves are converted into electric signals through piezoelectric transducer. Smart piezosensors allow one to detect the bone damage, and then perform the health control in the case of osteoporosis.

A very attractive idea is to use the movement of human organs to generate electricity, which can then be directed to stimulate the heart.[207] In this way, a pacemaker can be continuously loaded, and thus does not require an invasive battery replacement (which is usually performed *via* a surgical operation) (Fig. 14). Such self-charging can be provided by the work of one's heart, diaphragm or lungs at each breath.

In this case, piezoelectric transducers are implanted in the body, so they must not contain toxic heavy metals, which are often a component of piezoelectric ceramics. For example, PZT materials can contain Pb up to 50% by weight. Medical piezoelectric transducers are also made of polymers (PVDF and its copolymers) as well as polymeric composites. It was shown that the morphology of piezomaterials (grain size for ceramics or thickness of polymer film) influences their properties and defines the possibility of application.[208]

The use of continuous movements performed by various parts of the human's body to receive electricity, due to improved piezoelectric systems designed for medical purposes, is becoming one of the major challenges of modern electronic technologies. The practical use of such transducers in the form of implants requires biocompatibility and high durability of such devices during operation.

One can also mention the use of piezoelectric elements to monitor the work of the foot muscles, providing valuable information in the field of orthopedics, neurology, as well as in stress tests of sportsmen. Activity monitoring sytem can

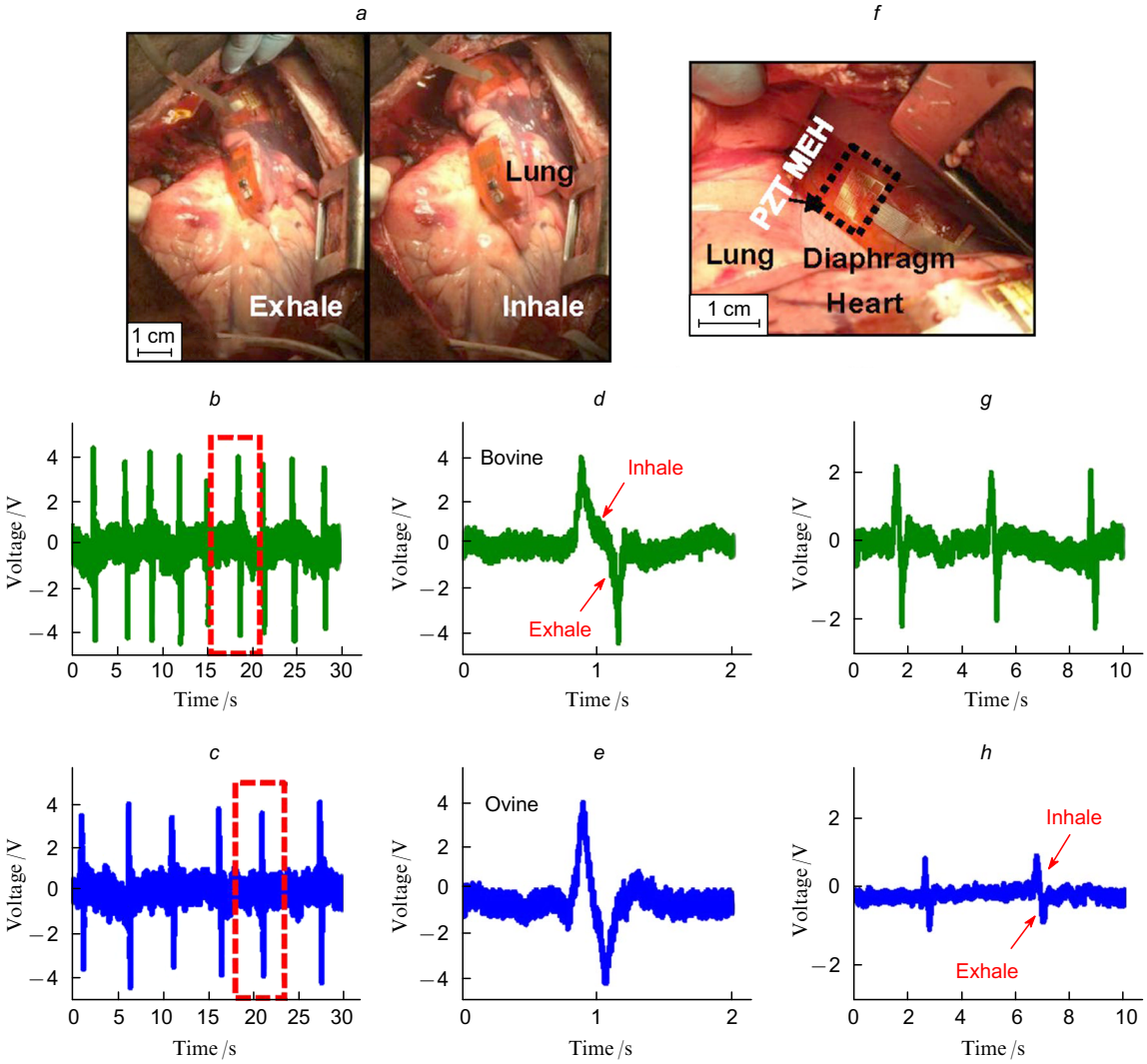


Figure 14. *In vivo* evaluation of lead zirconate titanate mechanical energy harvester (PZT MEH) on the lung and diaphragm. Image of a PZT MEH cointegrated with a microbattery and rectifier, mounted on the bovine lung (*a*). Voltage as a function of time for such devices on the bovine (*b*) and ovine (*c*) lungs. Plots *d* and *e* correspond to the regions indicated by the red dashed boxes in *b* and *c*, respectively. Image of a PZT MEH on the bovine diaphragm (*f*). Voltage as a function of time for such a device on the bovine (*g*) and ovine (*h*) diaphragm.[207]

help in detection of Alzheimer's or Parkinson's diseases at early stages.[209]

Piezoelectric materials using the work of human or animal muscles are not only the subject of research but also have already found practical application.[78]

The rapid development of tissue engineering in the last years contributed to the extension of the possibility of replacing sick or damaged human tissues with synthetic materials, including piezoelectric polymers. Live tissues (bones, cartilages, ligaments, skin, tendons) exhibit a natural piezoelectric effect, which plays a significant role in physiological processes. Thus, understanding these mechanisms is important for effective treatment. The piezoelectric properties of living systems inspired scientists to investigate synthetic substitutes for medical applications.

The majority of materials currently used for tissue regeneration represent only a mechanical support (scaffold) for tissues rebuilt in the healing process. Therefore, it has been found that the use of piezoelectric materials can further stimulate the proper growth of cells due to electrical pulses generated systematically as a result of the natural deformation (during the movement of living organisms).[171, 174, 211–213]

Such stimulation effect was observed in the case of bone and nervous cells and is very promising for purposes of biomedical engineering.[174] An undoubted advantage of using piezo-materials is the direct transfer of electric energy to the cells or damaged tissues without the need for an external energy source. Many interesting examples were reported by Rajabi *et al.*[174] and Ribeiro *et al.*[81]

Among polymers for these applications, PVDF plays a major role. This substance can be used in the form of films, membranes and fibres as wel as porous systems. PVDF-based scaffolds can be obtained by various methods such as solution or gel casting, precipitaion, emulsion freeze-drying, gas foaming, electrospinning or, recently, by rapid prototyping (3D-printing).[81] It is very important to obtain the appropriate morphology, particularly the proper porosity, necessary for colonization by living cells. Two strategies are generally accepted for tissue regeneration: implantation of a scaffold prepared from composites containing a piezoelectric polymer or growing cell cultures in bioreactors followed by their implantation.

The authors of the above-mentioned studies[81, 174] emphasize the importance of piezoelectric matrices used in tissue engineering, but they clearly indicate the need for further intensive research in order to improve their functionality because the mechanism of cell proliferation under electric stimuli is still unclear.

Apart from the biomedical devices described above, one can mention here the interesting proposal to use piezoelectric fibres for production of intelligent clothing.[214] Such fibres are embedded in a polymer matrix (PVDF and polyester) forming composite materials capable of recapturing, converting and storing of energy. The inserted energy of human hands can produce voltage outputs of up to 6 V, which corresponds to the energy of small batteries. The micropower generator thus formed was designed for gloves but probably it can be used for other human clothing. The efficiency of such device increases when multilayer structures are applied. This is an example of potential self-maintaining power supply.[214]

Wali[215] has proposed a very sensitive piezoelectric system to distinguish between different aromas from flowers.[215] Such device can detect aromatic volatiles directed to the polymer coated electromechanical resonator. This is a kind of an electronic nose, which can probably replace the subjective senses of people.

Recent studies demonstrated the possibility of 3D printing using piezoelectric materials. Chen *et al.*[189] has developed photocurable resin suitable for manufacturing piezoelectric products by this method. The authors optimized the composition of ink consisting of PVDF (piezoelectric component), 1,6-hexanediol diacrylate (monomer), diethyl fumarate (solvent ensuring proper consistency), UV absorber (Sudan I) and typical photoinitior (Irgacure) as well as the process conditions. It was found that various flexible PVDF-based 3D-products with high resolution ($\sim$7 μm) for sensing applications and biomedical detection can be manufactured by stereolithography.

3D-Printing has also been used to obtain inorganic nanoparticle–polymer composites with piezoelectric properties.[216] For this purpose, modified barium titanate nanoparticles were dispersed in poly(ethylene glycol) diacrylate solution. Formation of covalent bonds between nanoparticles and macromolecules under light irradiation resulted in improvement of piezoelectric properties ($d_{33} \sim 40$ pC/N). It was shown that interfacial layer and occurring interactions therein influence high efficiency of mechanical-electrical conversion and should be considered in design of piezoelectric materials.

The use of electrets for fabrication of microphones has been well known for many years. An interesting idea for such application is the use of a complex material SiO_2/Si_3N_4, obtained *via* low-pressure chemical vapour deposition (LP-CVD).[217] Hagiwara *et al.*[217] presented the original method of charging this material using soft X-ray radiation for the formation of electrets (Fig. 15).

It was found that such radiation causes ionization of a gas inside microphone, then ions are separated under applied electric field and negative charges are transferred to electrets. Moreover, the bias voltage determines the resulting surface potential.

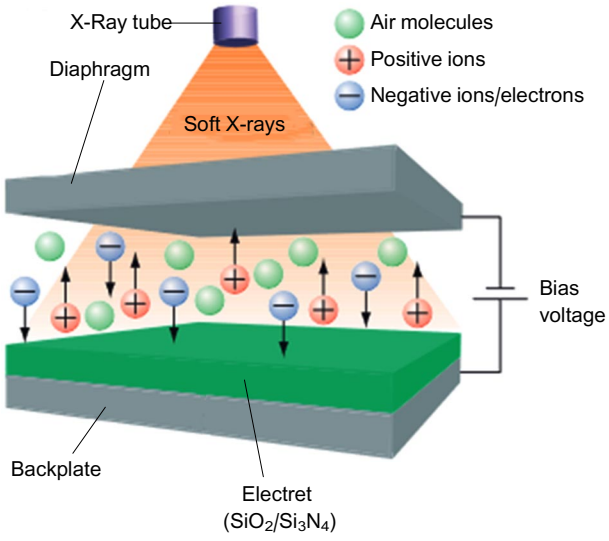


Figure 15. Conceptual diagram of charging method with soft X-ray irradiation for a silicon-condenser microphone.[217]

10. Conclusion

As demonstrated by the current researches, polymer piezoelectrics are materials with high potential finding increasing applications in modern microelectronics, medicine and science, due to a variety of their advantages that are not observed in ceramic materials. The most important among them are high flexibility, availability and low costs of raw materials, the possibility to use well-known processing methods as well as easy formability providing products of any shape and size. Moreover, their efficiency in generating electric current can be effectively improved by using appropriate technological processes (*e.g.* fibre electrospinning, orientation of plastic films) and modifications (by introducing appropriate fillers or copolymerization).

It should be emphasized that the use of piezoelectric polymers represents an alternative to inorganic compounds often containing toxic heavy metals (*e.g.* lead). Another environmental aspect is the use of piezoelectric biopolymers, which will help to reduce the production of petroleum polymers.

Basing on a review of scientific literature over recent years, it can be concluded that the search for novel piezoelectric materials derived from polymers, biopolymers and their composites with diverse, universal physicochemical properties relates to the expectations of modern technologists. However, due to the complexity of physicochemical processes occurring in piezoelectric materials, further studies are necessary to establish detailed correlation between the chemical microstructure/morphology of the samples and the ability to convert mechanical energy into electrical one and *vice versa*. The currently available sophisticated instrumental methods applied for the research and characterization of polymer piezoelectrics greatly increase our knowledge on these materials.

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