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Abstract

Recent advances provide new opportunities in the field of polymer piezoelectric materials. Piezoelectric materials provide unique insights to the fundamental understanding of the solid state. In addition, piezoelectric materials have a wide range of applications, representing billions of dollars of commercial applications. However, inorganic piezoelectric materials have limitations that polymer ferroelectric materials can overcome, if certain challenges can be addressed. This mini-review is a practical summary of the current research and future directions in the investigation and application of piezoelectric materials with an emphasis on polymeric piezoelectric materials. We will assume that the reader is well versed in the subject of polymers, however, not as familiar with piezoelectric materials.

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Introduction and Theory

Piezoelectricity is the ability of some materials to produce a surface charge when mechanical stress is applied; this is known as the direct piezoelectric effect. Conversely, these materials also produce mechanical strain when a voltage is applied, the so-called converse piezoelectric effect. A more formal definition is provided by the revised IEEE Standard on Piezoelectricity.[1] Piezoelectricity is inherently tied to the structure of the material, therefore providing unique insights into the solid state as well as an excellent testing ground for theoretical and computational predictions. Also, primarily due to the coupling of mechanical and electrical fields, they have a wide range of applications. Piezoelectricity was first reported in 1880.[2] In-depth treatments can be found in well-known books in the field. [3, 4, 5]

The linear constitutive equations describing piezoelectricity are:[1]

$T_{ij} = c^{E}{}_{ijkl}\, S_{kl} - e_{kij} E_k$ (Equation 1)

$D_i = e_{ikl}\, S_{kl} + \mu^{S}_{ij} E_k$ (Equation 2)

where; T_{ij} is Stress, S_{kl} is Strain, E_k is Electric field, D_i is the Electric displacement, $c^{E}{}_{ijkl}$ is the elastic constant, where the superscript indicates that the electric field is held constant, e_{ikl} is the piezoelectric constant, and μ^{S}_{ij} is the dielectric constant where the superscript indicates that the strain is held constant.

For equation 1, in the absence of an applied electric field, the term $e_{kij}E_k$ is zero, and equation 1 is simply a statement of Hooke's Law. For equation 2, in the absence of strain, the term $e_{ikl}\,S_{kl}$ is zero and equation 2 is simply the relation between electric displacement and electric fields for a dielectric material. In piezoelectric materials, the equations are coupled. A compressed matrix notation, also known as Voigt notation, is often used. The notation consists of replacing *ij* or *kl* by *p* or *q*, where *i, j, k, l* take the values 1, 2, 3 and *p, q* take the values 1, 2, 3, 4, 5, 6. Many alternate forms to the constitutive equations, equations 1 and 2, are available. However, care should be taken in interpreting them. One widely used form of equation 1 can be written as;

$$S_{ij} = s^E{}_{ijkl}\,T_{kl} + d_{kij}E_k \qquad \text{(Equation 3)}$$

where $s^E{}_{ijkl}$ is the elastic compliance constant, and d_{kij} is, unfortunately, also called the piezoelectric constant, or sometimes known as the piezoelectric strain tensor. The two constants, e_{ikl} and d_{kij} are related by equation 4.

$$e_{ip} = d_{iq}\,c^E{}_{qp} \qquad \text{(Equation 4)}$$

Referring to equation 3, if an electric field is applied along the z axis and the strain is measured along the same axis, a value for the d_{33} constant can be experimentally determined. For accurate results attention should be paid to the boundary conditions. For example, piezoelectric films are often clamped on a rigid substrate, and can expand or contract only in the direction perpendicular to the surface.[6] The d_{33} and/or d_{31} constant are typically reported in the literature as an experimental measure of displacement due to electric field. For high fields and strains, the linear

equations are not applicable and non-linear treatments are necessary. The reader is referred elsewhere for a discussion of non-linear piezoelectric materials.[7]

In many traditional inorganic piezoelectric/ferroelectric materials, such as $BaTiO_3$, the electric dipoles are due to relatively small ionic displacements and to a good approximation, the net polarization is the vector sum of these individual dipoles. However, the concept of individual molecular electric dipoles summing to give the macroscopic polarization is, in general, lost when molecules pack into a crystal lattice. This can be thought of as a renormalization due, in large part, to the electronic contribution. For example, in the case of polyvinylidene fluoride (PVDF) the dipole density would suggest a polarization of about 0.1 $\mu C/cm^2$, whereas the actual total polarization is nearly double that value when the electronic contribution is considered.[8] For a more extreme example, in the case of charge-transfer molecular ferroelectrics such as tetrathiofulvalene and *p*-chloranil,[9] essentially all of the polarization arises from the electronic contribution in the form of charge-transfer.

Density Functional Theory (DFT) is a powerful computational tool that can be used to model electronic structure and properties of materials from first principles, e.g. atomic structure and approximate solutions to the Schrodinger equation. Plane wave DFT uses periodic functions to model electron density in extended crystals, including the widely used Vienna Ab initio Simulation Package (VASP). Other popular plane wave DFT programs that have been used to model piezoelectric/ferroelectric tensors include ABINIT,[10] CASTEP,[11] CPMD,[12] NWChem,[13] and Quantum Espresso.[14] Alternatively, the solid state program CRYSTAL[15] uses atom-centered

orbital functions to calculate electronic materials properties. Piezoelectric effects are commonly modeled using density functional perturbation theory.[16] The electronic and ionic components of the system are assumed to be additive, and the *differences* between perturbed and non-perturbed systems are used, in accordance with the modern theory of polarization, presented by King-Smith and Vanderbilt.[17] The change in polarization ” p is described as a geometric quantum Berry phase,[18, 19] providing a proper quantum mechanical treatment of electric polarization. Resta offers a thorough review of the subject.[20, 21] This theoretical treatment is also consistent with experimental measurements, which essentially measure Δp rather than p, induced by an electric field. Applying the Berry phase method to the calculation of ferroelectric properties requires calculation of polarization (both ionic and electronic) for different input ion geometries and calculating the differences. In order to calculate piezoelectric properties, DFT methods are used to calculate the *changes* of the stress tensor with respect to changes in the applied electric field, or *changes* in the displacement electric field with respect to changes in the strain tensor to calculate the piezoelectric coefficients, *e* (differentials of equations 1 & 2, respectively). By distorting the matrix of atoms, the elastic constants are determined from the stress-strain relationship (see equation 1). Using the elastic constants and the piezoelectric coefficients *e* provided by the DFT code, equation 4 can be solved to determine the d_{33} values for comparison with typical experimental results. A collaborative online database of VASP calculations for piezoelectric properties is available; this database contains primarily inorganic materials and a few polymers.[22]

Related material properties:

A great number of material properties are closely related to piezoelectricity, including; Second harmonic generation (SHG), pyroelectricity, electroactive polymers, electrets and ferroelectricity. The connections between these material properties can be organized according to polar symmetries. First, we discuss true crystal classes, which are divided into 32 point groups representing all of the distinct Bravais lattices consistent with three-dimensional translational symmetry. Piezoelectricity is a property of 20 of the 32 point groups that lack inversion symmetry. Of the piezoelectric point groups, 10 are polar, meaning that they have a unique axis or polarization. The polar groups are also pyroelectric because a change in temperature will invariably change the polarization, if only because of thermal expansion. To extend the discussion to ferroelectricity, we go beyond crystal symmetry, which delineate what physical properties are possible, and consider the practical question of whether or not a polarization state can be reversed, or switched by application of an external electric field. This depends on the energy landscape in addition to the constraints imposed by symmetry.[23] In this sense, ferroelectricity is a subset of piezoelectricity. These two terms are sometimes used interchangeably, especially in the

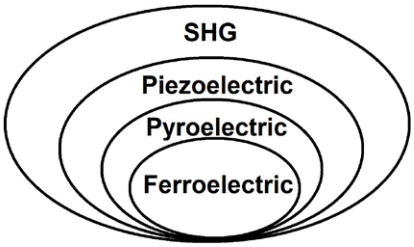


Figure 1: Hierarchal relation between key material properties related to piezoelectricity.

early literature, but this is to be avoided, especially in the case of molecular crystals, because few polar molecular crystals are ferroelectric, due to steric hindrance. Non-volatile computer random access memory (RAM) is an application of ferroelectricity[24] wherein the fundamental bistability of the ferroelectric state is essential. Well-known ferroelectric materials include Barium Titanate ($BaTiO_3$), and potassium dihydrogen phosphate (KDP) below 123K.

Pyroelectricity, as its name indicates, is the ability of some materials to produce an electric charge in response to changes in temperature; pyroelectric materials are also a subset of piezoelectrics (Figure 1). Pyroelectric materials such as Triglycine Sulfate (TGS) are used in infrared detectors.

Second harmonic generation (SHG) is another closely related material property, and all SHG's are piezoelectric. When an intense light source interacts with a SHG material, light at twice the original frequency can be created. This process is widely used in common green hand-held laser pointers to convert infrared light into visible green light. SHG is also used in communications for frequency mixing. In addition, SHG is used to image proteins.[25]

An electret material is a substance that has a metastable polarization arising from trapped charge, or metastable alignment of molecular dipoles, or both. The electromechanical response of electrets is similar to piezoelectrics. The direction of polarization may be changed at will without connection to the underlying structure. A drawback of electrets, is that the polarization is not stable and will relax over time, especially at elevated temperatures. This is in contrast to ferroelectric materials which exhibit true polarization bistability, which means that a ferroelectric

polarization state will not relax and can only be destroyed by heating above a characteristic ferroelectric ordering temperature, which can be very high for some ferroelectric materials (lead titanate, for one).

Electroactive polymers (EAPs) are polymers that mechanically respond to an external electric field. Piezoelectric polymers are a subset of EAPs in which the mechanism of response is piezoelectricity. Electroactive polymers usually achieve greater strains than inorganic materials, for example, because of their low elastic modulus. The low modulus, however, comes with at a price, EAPs typically produce less force than inorganic (or small molecule) piezoelectrics. For this reason, EAPs are more suitable for use with soft materials, where the low modulus results in good acoustic coupling in water or tissue, as for ultrasound and sonar applications. There are two main classifications of EAPs, dielectric and ionic. The dielectric EAPs typically rely on electrostatic forces. The ionic EAPs typically rely on the migration of ions. This often requires a fluid or gel. Some potential drawbacks of EAP's include drying out of the fluid or gel, slow response to external stimuli, and weak response, requiring higher operating current and power. Also, they do not always exhibit a true piezoelectric response, that is, the generation of charge when a force is applied. EAPs have current and potential biomedical applications, for example stapling devices.[26] Bar-Cohen[27] provides a review of EAP's. The annual EAP conference[28] promotes an artificial muscle competition.[29]

Charged cellular polypropylene, also known as void films, are another approach to EAP's.[30] Voids within of the cellular polymer are charged by applying a high voltage to the structure. This

generates internal dielectric barrier microdischarges. Because of this phenomenon, the deposited charges on the internal surface of the voids create electrical polarization, an electret effect with piezoelectric-like properties.[31] Ramadan *et al*.[32] provide a review of piezoelectric polymers, particularly micro-electro-mechanical systems (MEMS) applications.

Applications

Sonar was one of the first applications of piezoelectricity in 1916.[33] However, one of the most widely used applications of ferroelectric/piezoelectric materials is in high-Q capacitors, also commonly called ceramic capacitors. Interestingly, this application does not directly exploit the materials' piezoelectric or ferroelectric properties. Instead, the increase in the dielectric constant near the Curie point (temperature at which a polar phase transitions to a non-polar phase) creates the high dielectric constant, and hence the enhanced capacitance. Doped barium titanate, $BaTiO_3$ is widely used in capacitors. Doping broadens the sharp temperature dependence of the dielectric constant on temperature.[34] In a related application, piezoelectric materials were studied as high-k gate insulators (insulators with a high dielectric constant, k) in response to the scaling problem in field effect transistors (FET)s.[35]

A solid solution ceramic, lead zirconate, $PbZr_xTi_{1-x}O_3$, commonly called PZT, was discovered in 1951.[36] It is one of the most widely used piezoelectric materials, even today. A nearly vertical morphotropic phase boundary (MPB) between polar rhombohedral and non-polar tetragonal crystal structures(see Figure 2), enhances its dielectric and piezoelectric response because close to the MPB, the energy surface for polarization is very flat.[37]

Ceramics like PZT almost always need to be poled. Poling is the process of aligning polar domains to the extent possible by applying a large DC electric field and/or lowering through paraelectric-ferroelectric transition temperature while a DC electric field is applied. Polymer piezoelectric materials, are often poled as well. Ceramic piezoelectric materials can typically produce large stresses, forces and/or pressures, but are limited to very small strains and/or displacements, due to the high elastic moduli of these materials. Various strategies have been implemented to trade the high stresses for larger displacements, including: Mechanically amplified actuators such as "cymbal" (named due to its similar shape to the musical instrument), and composites such as; RAINBOW (reduced and internally biased oxide wafer),[38] CRESCENT (stress-biased ceramic-metal composite actuator),[39] LIPCA (lightweight piezocomposite curved actuator),[40] MOONIE (moon-shaped actuator),[41] and THUNDER (thin-layer composite unimorph ferroelectric driver and sensor).[42]

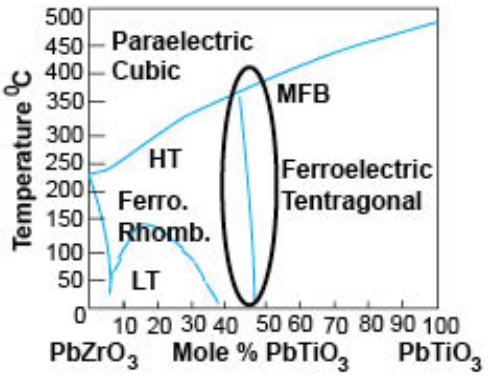


Figure 2: Phase diagram for solid solution ceramic, lead zirconate, PbZrxTi1− xO3 showing a nearly vertical morphotropic phase boundary. Adapted from Jaffe et al. Ref 4.

Figure 3 provides a qualitative comparison of force vs. displacement between various actuator designs.

Energy harvesting is a large and growing application of piezoelectric materials.[43, 44, 45, 46] Other applications include surface acoustic waves (SAW) devices, spark igniters, ultrasonic motors, medical ultrasonic applications,[47] audio speakers, buzzers, robotics,[48] and morphing aircraft wings[49] to name but a few. The list of applications is even longer when associated phenomena, such as ferroelectricity is considered.

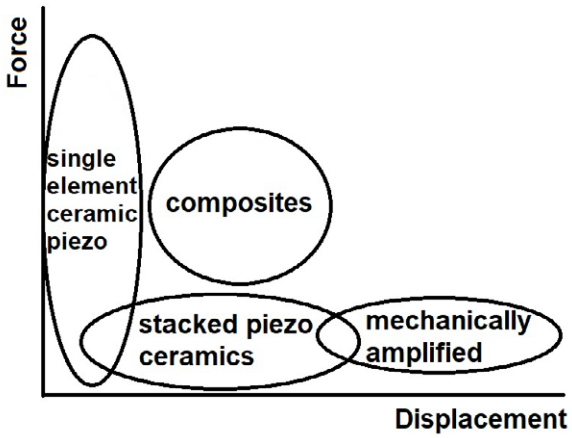


Figure 3: Qualitative comparison of popular actuator designs emphasizing the tradeoff between force and displacement.

For practical engineering applications, finite element analysis (FEA) numerical simulations are a useful tool, particularly for objects with complex geometries. FEA is an engineering tool that predicts how a material reacts under real world conditions, by using small "elements" such as cubes of the material to predict how the material behaves macroscopically. ANSYS and

COMSOL are popular commercial FEA packages. FEA packages are frequently used with computer aided design (CAD) software. Typically, a CAD model of an object is created. The object is then parsed into many elements. Specific parameters are input into the model, such as boundary conditions, any applied forces, temperatures, electric field, etc. and material properties of each material used. The appropriate physics equations are solved for each element. The element solutions are then matched at the interfaces between elements creating a patchwork solution. In piezoelectrics, due to the interaction of the mechanical and electrical fields, more advanced FEA known as multiphysics FEA is required. In addition, many actuator applications have high aspect ratios, further complicating the analysis.[50]

Experimental techniques

There is a wide range of experimental techniques for characterizing piezoelectric and/or ferroelectric materials. We will mention only a few here, specifically techniques which use (1) direct observation of materials changes upon application of an electric field, (2) observation of phase changes thermally, and (3) piezoresponse force microscopy. Strain response to applied electric fields are perhaps the most direct measurement of the piezoelectric response; these are reported as "butterfly curves", see Figure 4,.

Samples are prepared by affixing conductive electrodes to opposite sides of the sample, forming

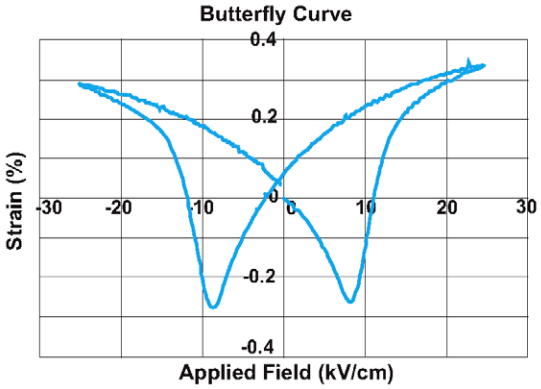


Figure 4: Typical piezoresponse "Butterfly" curve for PZT. Thickness 0.9 mm, Area = 1.26 cm^2.

a parallel plate capacitor. If the sample has a high dielectric constant, close contact between the sample and the electrode is critical. For example, even a small gap would result in most of the applied voltage being dropped across the gap rather than the sample. Silver or gold paint, or vapor deposited gold electrodes are commonly used. Numerous articles have been written on the electrode-sample interface.[51, 52] The electrodes are used to apply an electric field while the surface displacement is monitored, usually with a fiber optic sensor, linear variable differential transformer (LVDT), laser micrometer, or similar device.[53] From this measurement, the value of one of the components of the piezoelectric tensor, d_{33} in this case, can be determined using equation 3. A measurement of the lateral surface displacement can be used to determine off-diagonal components of the piezoelectric tensor, d_{31}, in this case. Quite often a ferroelectric hysteresis response can be acquired simultaneously. The most widely used acquisition circuit for measuring ferroelectric hysteresis is a modern modification of the Sawyer Tower[54] circuit. In the modern circuit a virtual ground operational amplifier circuit is used to sum the current flowing onto/off the sample electrodes. In the early days, false reports of ferroelectricity were common, primarily due to artifacts such as resistive and/or linear capacitive responses being falsely identified as ferroelectric. Scott[55] provides a whimsical article on false ferroelectric responses from the skin of a banana. Recently reports of false ferroelectric responses have been connected with reporting multiferroic materials,[56] that is, materials with both magnetic and electronic polarizations. Some modified Sawyer-Tower systems are available commercially, for example, Radiant Technologies and Advanced Customized Characterization Technology.

Piezoelectric (and ferroelectric) materials undergo a structural phase transition at the Curie point. This typically results in a sharp peak when the capacitance is measured as a function of temperature, measured with electrodes similar to those described above, as temperature is varied. In a related measurement technique, differential scanning calorimetry (DSC) measures the heat flowing into or out of a sample as a function of temperature, and shows a similar discontinuity at the Curie point. Sherrit and Makherjee[57] review characterization techniques for piezoelectric materials for transducer applications, with a particularly thorough review of frequency dependent issues such as impedance.

Piezoresponse Force Microscopy (PFM), an adaptation of Atomic Force Microscopy (AFM), was first introduced in 1992,[58] and has become widely used for detecting piezoelectricity, particularly in thin films. PFM only requires a bottom electrode be affixed to the sample. A conductive PFM cantilever acts as the top electrode. Two methods are typically employed: a single point measurement or a scanning methodology. In the case of the single point method, the x-y motion of the sample is arrested and an AC signal is applied across the sample. Simultaneously a DC voltage sweep is applied to the sample ranging from some negative voltage to a positive voltage and then sweeping back down to the original voltage. Two electrical responses are collected simultaneously from the cantilever. One is the detector current or amplitude, which, with proper calibration, can be converted to strain. The other response is the phase between the applied AC signal and the response. The product of the amplitude with the cosine of the phase yields an unfolded butterfly curve, resulting in a hysteresis loop (see Figure

4). This is often referred to as the piezoresponse. In the scanning method, x-y scans are taken while typically monitoring three sample responses: surface height, polar phase, and polarization magnitude, looking for evidence of ferroelectric domains. Of course, the height response should not show any domain structure and is primarily used for comparison to distinguish surface features from domains. Figure 5 shows a PFM image of periodically poled lithium niobate (PPLN) substrate. PPLN is a commercially available ferroelectric material (used in SHG applications), making it a nice standard for PFM. As an extension of the scanning method, a strong DC field can be applied across the sample to write domains. The domains are later read using the previously described scan technique. See Figure 6.

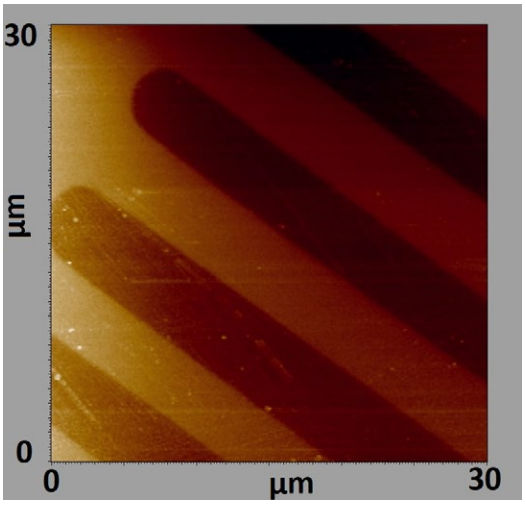


Figure 5: PFM image (phase) of a PPLN standard showing diagonal ferroelectric domains.

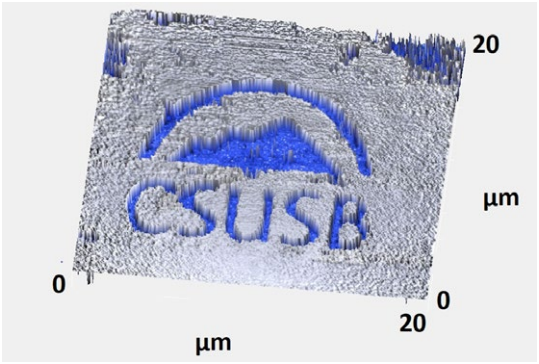


Figure 6: (CSUSB logo) written in ferroelectric BaTiO3 by applying a voltage using a conductive AFM thereby selectively arranging domains and later reading those domains with the AFM.

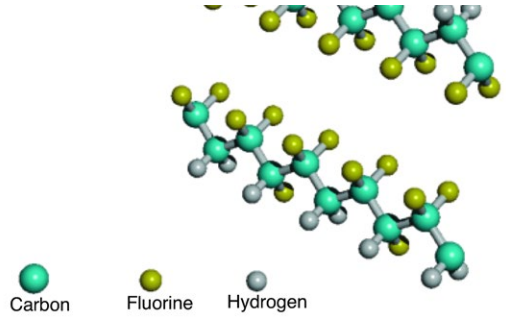
While imaging native polar domains and reading/writing polar domains might be taken as convincing evidence of ferroelectricity, they are not always conclusive. Several publications have addressed false positive data obtained in this manner.[59, 60, 61] One of the primary sources of false positive piezoelectric responses is due to the electrostatic force between the cantilever and the sample. This tends to stretch the piezoresponse curve. Another primary source of false positives is charge injection. A modified contact Kelvin probe force microscopy (cKPFM) measurement is an effective tool for distinguish false results from genuine ferroelectric responses.[62] Recently a technique which utilizes the direct piezoelectric effect (dPFM) has been reported.[63] Incidentally, piezoelectric actuators are used in AFMs; They are an integral part of the x-y-z motion control, as well as the cantilever[64] in some cases.

Polymers

One of the main challenges to applications of inorganic piezoelectric materials is that they are typically brittle. Attempts have been made to overcome this challenge. For example, ribbons of PZT are sandwiched between poly (4,42oxydiphenylene pyromellitimide), (commonly known as Kapton™) in a construction known as Microfiber Composites,™ commercially available from Smart Materials. Another approach combines the complementary properties of ceramic piezoelectric materials with polymers by dispersing ceramic particles in a polymer. Sampathkumar *et al.*[65] review ceramic inclusions randomly dispersed in a polymer matrix, known as 0-3 connectivity.

The discovery of piezoelectricity in polyvinylidene fluoride (PVDF)[66] in 1969 revolutionized the field of soft piezoelectric materials. However, ferroelectricity in PVDF was not accepted until about 1980, following a study of the copolymers, e.g. PVDF-TrFE (PVDF-trifluoroethylene), which allowed careful study of the phase transition (Figure 7). Without characterizing a phase transition accompanying a change in piezoelectricity, it was not possible to rule out electret effects in what were fundamentally polymorphous materials.[23] Kepler and Anderson[67] provide an early review (1992) of ferroelectric polymers. Harrison and Ounaies[68] provide a 2002 review, and Fukada[69] presents a review of piezoelectric polymers up to 2006. Three different crystalline phases have been identified in untreated PVDF: ±, ², and ³. The ² -phase, which is useful for piezoelectricity, can be obtained by mechanical stretching and electrical polarization.[31] Compared to traditional ceramic piezoelectric materials, polymer piezoelectric materials are much more flexible and easier to produce. However, they have some disadvantages. Their d_{33} values are smaller and they require a comparatively large external electric field, known as the coercive field, to reverse the polarization. Much of this is due to an important distinction between the polarization reversal mechanisms in polymers, versus inorganic materials, in which the reversal proceeds via

Figure 7: Structure of PVDF-TrFE showing the all-trans conformation and parallel crystal packing of the ferroelectric phase.



relatively small ionic displacements or ordering. In the case of known polymer materials, significant rotation of the polymer change is required.[23]

Typically, coercive fields for polymers (5 x 10^7 V/m for PVDF) are greater than those for inorganics (2.4 x 10^7 V/m for PZT). However, thin polymer films require less applied voltage to produce the necessary coercive fields. Several different methods for producing piezoelectric polymer films can be employed: replica molding, spin coating, electrospinning, casting, screen printing and more recently, nanoimprinting lithography and photolithography. Ramadan *et al.*[70] provide an overview in Table 2 of their manuscript. The Langmuir-Blodgett (LB) method can be used to produce particularly thin films (~15 nm)[71] with high crystallinity, with polarizations oriented perpendicular to the film. The effective d_{33} values of films prepared in this manner can be as high as 20 pm/V.

The problem of fatigue (decrease in polarization with increasing number of polarization reversals)[1] has long plagued ferroelectric materials in the application of non-volatile memory. This continues to be a challenge for inorganic ferroelectric materials as well as polymer ferroelectric materials. Polymeric materials also lose activity due to aging. For example, the remnant polarization in PVDF-TrFE significantly decreases upon 10^6 switching cycles, which is significantly lower than the 10^8 cycles desired by industry standards.[72] In contrast, inorganic oxide memory devices currently used commercially can achieve 10^{12} switching cycles or more.[73] Nylon 5, 7, 9 and, 11 are also classic piezoelectric polymers, forming electric dipoles due to

hydrogen bonding.[74] As an example, the structure of hydrogen bonding in Nylon 11 is shown in Figure 8 and its piezoelectric properties are listed in Table 1.

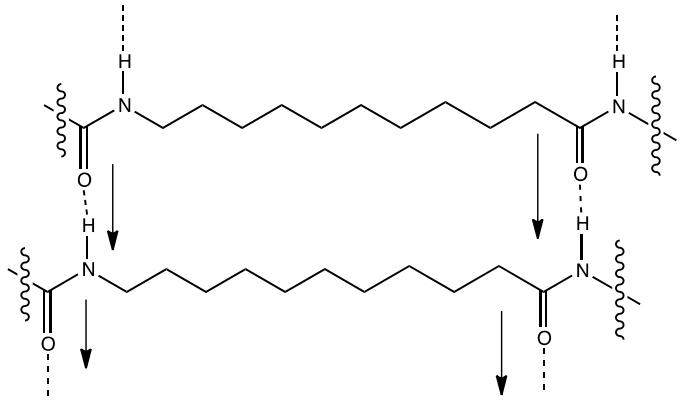


Figure 8: Dipole moment of Nylon 11.

Other piezoelectric polymers also have been reported, such as polyvinyl chloride (PVC) and (PVDCN) copolymers; the latter was reported to have a saturation polarization of 5.5 μC/cm^2, comparable with that of PVDF.[75]

Table 1: Comparison between, polymeric inorganic, and single molecule piezoelectric materials.

Properties	PVDF	Nylon 11	PZT	BaTiO3	Croconic acid
Density (g/cm^3)	1.78	1.15	7.5	6	1.912
Piezoelectric constant (d_{31}) (pC/N)	up to 23	3 to 14	170 to 270	78	n/a
Piezoelectric constant (d_{33}) (pC/N)	up to 30	2	up to 220	up to 100	5
Saturation Polarization (μC/cm^2)	5 to 8	5 to 8	20 to 40	up to 26	20
Coercive field (V/m)	5 x 10^7	1 x 10^8	2.4 to 14.4 x10^5	4.5 x 10^5	11 to 29 x 10^5

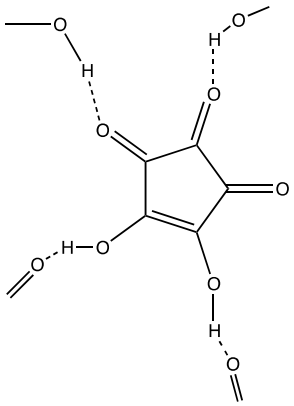
Note: Absolute values for d_{31} and d_{33}

Piezoelectric polymers, particular PVDF and its copolymers find many applications in technology and industry. For instance, these piezoelectric polymers are fabricated as tactile sensors detecting force and temperature changes[76, 77] and are used as acoustic transducers transmitting electromechanical signals,[78] applied robotics and in the medical field. Piezoelectric polymers can also be used to harvest vibrational energy by transforming mechanical energy into electricity.[79, 80] In addition, certain piezoelectric synthetic polymers are compatible with biological tissue. Many tissues, such as collagen, keratin, fibrin and prestin etc., are themselves piezoelectric. [81, 82, 83] PVDF and vinylidene fluoride (VDF) copolymers provide good candidates in electromechanical transduction for tissue engineering due to their large piezoelectric response, as well as biological stability. For example, PVDF fibers were tested as scaffolds in a bone tissue engineering application, and its effect on biological function was investigated with human mesenchymal stem cells. [84, 85] A mixture of PVDF and polyurethane was studied for its piezoelectric effect on wound healing and fibroblast activity.[86] Other than PVDF, poly-L-lactic acid (PLLA), a biodegradable polymer which demonstrates piezoelectricity[87] was used as a bone substitute that was approved by US Food and Drug Administration.[88] Recently, PLLA was incorporated with other bioactive materials such as hydroxyapatite and collagen to grow fetal osteoblasts and endothelial cells derived from human stem cells.[89, 90] Most research on the application of PVDF and other piezoelectric biopolymers is focused on bone collagen. Despite a well-established biophysical model for prestin's electromechanical activity, no synthetic

piezoelectric polymers have yet been incorporated into this tissue, in part due to the unclear molecular mechanisms underlying prestin's piezoelectric activity.[91]

Current research:

Recent discoveries of room temperature organic and organometallic piezoelectric materials with activity comparable to inorganics have reignited an interest in organic/organometallic piezoelectric materials. Most notable are croconic acid[92] (Figure 9), and diisopropylammonium bromide[93, 94] (DIPAB, Figure 10). Croconic Acid has a saturation polarization of 20 μC/cm^2 and a Curie temperature above its molecular decomposition temperature (450 K). Crystalline croconic acid is hydrogen bonded, and its mechanism for ferroelectric reversal is through hydrogen bond transfer cascades. Incidentally, squaric acid (SA), the 4-carbon analog of CA, has been known as an antiferroelectric (a material with local dipoles that are cancelled out by adjacent dipoles) for years. SA is an example of an organic compound that undergoes phase transition similar to the well-known piezoelectric, potassium dihydrogen phosphate (KDP). Diisopropylammonium Bromide has a saturation polarization of up to 23 μC/cm^2 and a Curie temperature of 426 K, well above room temperature. This new generation of organic and organometallic piezoelectric and ferroelectric materials has not yet been deployed in applications.



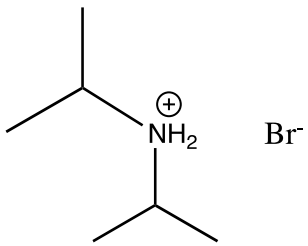


Figure10: diisopropylammonium bromide (DIPAB)

Figure 9: Croconic Acid:

Future directions.

Multifunctional materials hold great promise both for increasing the fundamental understanding of materials and for novel applications. Piezoelectric materials are perhaps the most familiar examples of multifunctional materials, linking mechanical and electrical fields. Multiferroic materials that link ferroelectricity and ferromagnetism have a wealth of potential applications. One potential application would be computer data storage devices that could be written to electrically and read magnetically, or *vice versa*. An even more exciting prospect would be magnetoelectric materials in which static electric fields and static magnetic fields interact. This would contrast to the now common electromagnetic interaction of changing electric fields and changing magnetic fields that is at the heart of our current technologies (i.e. electric motors, generators, radio waves, etc.). From a theoretical standpoint multiferroic materials provide intellectually stimulating challenges. At one time, ferroelectricity and ferromagnetism were believed to be mutually exclusive, due primarily to the observation that in common perovskite ferroelectric materials of the form ABO_3, ($BaTiO_3$ being the most common), bonding results in

no unpaired d electrons, and hence a lack of ferromagnetism. Substituting Mn for Ti in the complex, allows for the possibility of both ferroelectricity and ferromagnetism. Based on this, $BiMnO_3$ was predicted and subsequently shown experimentally to be ferroelectric with ferromagnetic ordering.[95, 96, 97]

Magnetoelectric nanocomposites are made up of discrete regions of ferroelectric and ferromagnetic materials, bonded together. Magnetoelectric responses that are orders of magnitude greater than what is typically found in single-phase materials have been reported.[98] The magnetic-electronic interaction is facilitated by mechanical intermediaries; piezoelectricity and magnetostriction (the magnetic analog of piezoelectricity). In these composites, for example, the application of an electric field produces a mechanical stress in the piezoelectric region, which in turn produces a magnetic field in the mangnetostriction region. Typically, these discrete regions are in the form of layers.[99] An alternate approach is core-shell nanocomposites with a ferroelectric "coat" surrounding magnetic nanoparticles forming a 0-3 dimension nanocomposite. The literature contains examples in which a ferroelectric polymer matrix (PVDF or related) is used in combination with various magnetic nanoparticles.[100, 101, 102] A particularly thorough review article was published by Martins and Senentxu.[103]

A topical review article[104] is focused on the multiferroic system, applied to spintronics, where the ferromagnetism in the (Ga, Mn)As diluted magnetic semiconductors (DMS) ferromagnetic channel is controlled by the non-volatile field effect of the ferroelectric spontaneous polarization.

Use of ferroelectric polymers as gates in such heterostructures offers a viable alternative to the traditional oxide ferroelectric materials, which are generally incompatible with DMS.

Conclusions:

Recent advances, particularly in the area of inorganic/organic-organometallic piezoelectric materials, may prompt new interest in piezoelectric materials by polymer scientists. There is untapped potential in heteropolymers, copolymers, and polymeric/embedded materials. Hopefully this primer has provided a starting point for understanding the history, theory, experimental practices and applications of piezoelectric materials.

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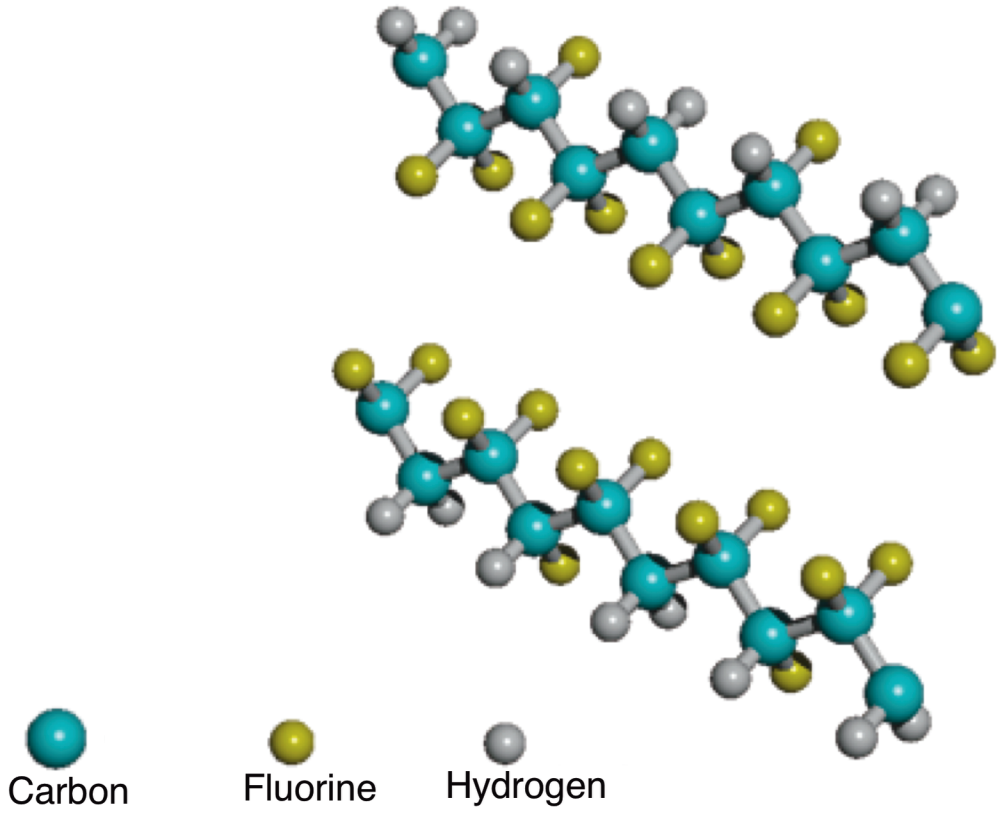

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Recent advances provide new opportunities in the field of polymer piezoelectric materials. Traditional inorganic piezoelectric materials have limitations that polymer ferroelectric materials can overcome, if certain challenges can be addressed. This mini-review is a practical summary of the current research and future directions with an emphasis on polymeric piezoelectric materials.