

# Organic Piezoelectric Wearable & Implantable Sensors

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## Abstract

Piezoelectric properties, capable of transforming mechanical stress into an electrical potential, or vice versa, are currently being explored for wearable and implantable sensor applications. The historical focus of studies has centered around inorganic materials systems. However, attention has recently shifted to organic piezoelectric materials, with an interest in the biocompatible and biodegradable properties for biomedical applications. The applications hold promise as a more sustainable and ideal alternative to the current industry-standard sensors. This paper explores the current understanding of organic piezoelectric materials, ongoing research into biomedical applications in sensor technology, and specific examples of current sensor prototypes.

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## 1. Introduction

Quartz was the first piezoelectric material to be discovered by the Curie brothers in the late 1800s. Interest in piezoelectricity and its sonar technology application increased following the sinking of the Titanic. That incident, combined with the outbreak of World War I, resulted in a serious push for research into piezoelectric materials and sonar technology. The only known piezoelectric materials at the time, quartz and Rochelle salt, were used in the development of sonar technology. Quartz devices relied on single crystals and their size was limited by available processing techniques. Rochelle salt was limited by temperature dependence and sensitive to humidity and dryness. Post-WWI research continued to search for different piezoelectric materials that were more reliable than quartz and Rochelle salt [1]. Since then, numerous piezoelectric materials have been discovered. Notably, barium titanate (BTO), lead zirconate titanate (PZT), and polyvinylidene fluoride (PVDF) have advanced the understanding and usage of piezoelectric materials. Today, piezoelectric materials have applications in a variety of industries, ranging from tires to biomedical devices, speakers, and robotics [2].

In recent years, interest in organic piezoelectric materials has increased due to their biocompatibility, flexibility, sustainability, and processability [3]. Organic piezoelectric materials can often be processed without solvents and heavy metals, thus offering an environmentally friendly option. Additionally, they don't require specific, high-energy conditions to be processed [4]. In particular, research into organic piezoelectric biomaterials has focused on device applications in the biomedical field. The biomedical microelectromechanical system (Bio-MEMS) devices range from pressure sensors to measure respiration, vibrations in the vocal cord, and artery pressures, to actuators and tissue regeneration stimulators. Prospective biodegradable sensors could reduce the need for excess invasive surgeries as sensor removal is no longer needed. Additional flexibility in sensors would assist with detailed health monitoring devices. However, before implementation into industry practice, researchers must overcome organic material's weaker piezoelectric effect compared to their inorganic counterparts [3], [5]. This paper reviews the theory behind piezoelectricity in inorganic and organic materials and delves into different organic piezoelectric materials and their associated wearable and implantable sensor technologies.

## 2. Piezoelectricity

Piezoelectricity, derived from the Greek root “piezo” meaning “pressure”, directly translates to pressure electricity [1]. Piezoelectric materials convert mechanical deformations into electrical energy [5] with the strength of the piezoelectric response represented through the calculated piezoelectric coefficient,  $d_{ij}$ . The piezoelectric coefficient subscript  $i$  represents the direction of the applied stress, either normal or shear, while subscript  $j$  represents the resulting charge per unit area in the  $j$  direction [3], [6].

Piezoelectric materials are divided into two categories: inorganic and organic. The formation of the piezoelectric effect differs between these two types of materials. Due to this and the crystalline structure of the materials, the piezoelectric constants vary between materials. Inorganic materials tend to have higher piezoelectric coefficient values compared to organic materials. **Table 1** summarizes the normal piezoelectric and shear piezoelectric coefficients for several common organic and inorganic materials.

## 3. Inorganic Piezoelectric Materials

When an inorganic piezoelectric material experiences a mechanical force that results in a deformation, a shift in the crystal structure occurs. This dislocation causes a shift in the ions, inducing a dipole moment within the inorganic solid. Inorganic materials must be noncentrosymmetric in order to show piezoelectric properties. A center of symmetry within a crystal structure would cause any induced dipole moment to be canceled out [5]. Inorganic piezoelectric material examples include perovskite ceramics such as lead zirconate titanate ( $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ , PZT), barium titanate ( $\text{BaTiO}_3$ ), lithium niobate ( $\text{LiNbO}_3$ ), and semiconductors such as gallium nitride

**Table 1.** Normal and shear piezoelectric constants for common organic and inorganic piezoelectric materials.

Materials	Normal Piezoelectric Constant	Shear Piezoelectric Constant	Source
<b>Organic Piezoelectric Materials</b>			
Collagen	$d_{33} = 2.64$ pC/N	$d_{14} = .02-2.0$ pC/N	[7], [8]
Silk	—	$d_{14} = -1.5$ pC/N	[9]
Glycine ( $\beta$ -phase)	—	$d_{16} = 178$ pm/V	[10]
Glycine ( $\gamma$ -phase)	$d_{33} = 9.93$ pm/V	—	[10]
PLLA	$d_{33} = 6-12$ pC/N	—	[11]
PVDF	$d_{33} = -33$ pC/N	—	[12]
<b>Inorganic Piezoelectric Materials</b>			
ZnO	$d_{33} = 6-13$ pc/N	—	[12]
Graphene	$d_{33} = 1.4$ nm/V	—	[13]
GaN	$d_{33} = 3.1$ pm/V	—	[14]

BaTiO <sub>3</sub>	$d_{33} = 191$ pC/N	—	[15]
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(GaN), and zinc oxide (ZnO) [5], [16]. Some inorganic piezoelectric materials are biocompatible, such as  $\text{BaTiO}_3$ ,  $\text{LiNbO}_3$ , and potassium sodium niobate (KNN) [5], while some, including  $\text{LiNbO}_3$ , PZT, and ZnO can become biocompatible through processing techniques [11]. However, these materials lack biodegradability. Sensor biodegradability eliminates the need for additional surgeries for device removal and the associated costs and risks. This property has become increasingly important as the research focus shifts to piezoelectric biomedical applications.

## 4. Organic Piezoelectric Materials

While inorganic piezoelectric materials rely on the shifting of the atoms within a crystal structure, organic piezoelectric materials depend on the molecular dipoles in the material reorienting [3], [5]. This is possible through the presence of permanent molecular dipoles within the material that can keep the reorientation. Popular organic materials being investigated for their piezoelectric properties include glycine [17], collagen, and silk (synthetic spider silk [18]).

Glycine, in particular, has generated interest as a piezoelectric material. Glycine has three phases ( $\alpha$ ,  $\beta$ , and  $\gamma$ ). Glycine’s  $\alpha$ -phase’s centrosymmetric structure causes the dipoles to cancel, negating any possible piezoelectric effect. However, the  $\beta$ - and  $\gamma$ -phases, without a centrosymmetric structure, produce dipoles that result in a piezoelectric effect (see **Table 1**) [17].  $\gamma$ -phase glycine has a relatively high normal piezoelectric coefficient  $d_{33}$  of 9.93 pm/V. Likewise,  $\beta$ -phase glycine also had a high shear piezoelectric coefficient  $d_{16}$  of  $178 \pm 11$  pm/V [10]. The high piezoelectric constants, combined with glycine’s biodegradability, make it an ideal candidate for biomedical applications.

Another organic piezoelectric material being investigated for future applications is collagen. Collagen is already incorporated into numerous FDA-approved biomedical devices and thus is easier to incorporate into new devices [19]. Collagen’s piezoelectric effect utilizes the dipole moment created from the reorientation of its charged and polar groups along the molecule’s longitudinal axis [5]. Collagen’s shear piezoelectric coefficient of  $d_{14} = .02-2.0$  pC/N [7] is relatively small, however, the piezoelectric coefficient can be increased through the addition of chitosan [5]. The chitosan aligns the collagen fibers, improving the piezoelectric effect [17]. Additionally, collagen is biodegradable, being completely degraded *in vivo* in approximately 3 months. The degradation time can be adjusted by tuning the amount of cross-linking present in the collagen [19]. Due to its combined piezoelectric and biocompatible properties, collagen shows promise in flexible and implantable sensors [20].

Additionally, silk is being investigated for its possible usage in biomedical applications, as a piezoelectric effect is created from silk’s crystalline phases and orientation [5]. Specifically, the combined increased presence of  $\beta$ -sheet crystallinity and orientation results in an increased piezoelectric effect [9]. With silk technology already implemented into the medical industry, including bone

regeneration and tissue engineering [5], it holds promise for integration into silk-based sensors. Silk's shear piezoelectric constant of  $d_{14} = -1.5$  pC/N [9] and biodegradability make it a promising candidate for implantable medical devices. A silk film can dissolve in approximately 30 seconds in DI water [21] and silk scaffolds can degrade within 2-6 months *in vivo* [2]. The degradation time and behavior can be adjusted through the processing technique or with a post-treatment process that alters the crystallinity of the silk [2], [21]. Synthetic spider silk in particular is being investigated for its piezoelectric properties. With a normal piezoelectric coefficient of  $d_{33} = 3.62$  pC/N, the synthetic spider silk also demonstrated cyclical electrical resistivity in differing humidities. This, combined with synthetic spider silk's elasticity, makes it a strong candidate for silk nanofibers implementation in nerve cell regrowth, drug delivery [18], and Bio-MEMS devices.

## 5. Piezoelectric Sensors

The application of organic piezoelectric biomaterials has generated significant interest from the biomedical field. This is mainly due to the prospect of biocompatible and/or biodegradable technology that the organic characteristic of piezoelectric materials will introduce. Recent investigations into organic piezoelectric materials have revolved around the topic of wearable and implantable sensors. Sensors convert the piezoelectric signal generated by the mechanical deformation into interpretable data. Piezoelectric technology integration into sensors has long been researched as a way to increase current sensors' wearability and flexibility. These attributes allow for more specialized health monitoring and better diagnostic abilities [5].

Inorganic piezoelectric materials have previously been investigated for their applications in sensors. Unfortunately, the majority of inorganic materials with a strong piezoelectric effect, like PZT, are toxic. This makes it difficult to apply within the biomedical field. However, ZnO nanostructures are one example of an inorganic piezoelectric material used to create a sensor [22]. Zinc-oxide has a piezoelectric coefficient of  $d_{33}$  that ranges from 6-13 pC/N [12]. While ZnO nanostructures are biocompatible and can rapidly respond to dynamic stimuli without consuming a lot of power, they lack the flexibility of wearable sensors [22]. This is where sensors from organic piezoelectric biomaterials have the benefit of biodegradability and flexibility [3].

### 5.1. Wearable Sensors

Wearable, noninvasive sensors, also referred to as electronic skin or e-skin, are desirable due to their potential benefits for health monitoring and diagnostics [5]. Glycine, with its high piezoelectric constant and biocompatibility and biodegradability, is being tested in pressure sensors. One prototype combined the  $\beta$ -phase glycine with chitosan utilizing an environmentally friendly room temperature, water-based process. Chitosan, also a biocompatible and biodegradable polymer, was paired with glycine to create a

pressure sensor that, when actuated, generated a voltage output of 190 mV for a duration of 9000 cycles. This glycine-chitosan composite sensor displays promising durability and biodegradability. These attributes, along with ease of fabrication, could be applied to creating environmentally-friendly biomedical pressure sensors [17].

Silk can also be used for wearable sensors. One pressure sensor example used dual water treatments to align the fibers and assist the polarization of the spider silk. When tested, the sensor was found to output 21.3 volts, a current of 0.68  $\mu$ A, and had an energy conversion efficiency of 66%. The potential applications of this wearable sensor include monitoring and measuring pulse and throat movements generated during speaking, drinking, or coughing [23].

Lastly, one prototype e-skin used fish gelatin electrospun nanofibers to create a pressure sensor. This experiment yielded a piezoelectric constant of  $d_{33} = -20$  pm/V, allowing it to be self-powered for 108,000+ stability test cycles over 6 months [24]. Another example of a flexible sensor designed to mimic human skin used the collagen fibrils in fish skin to create a piezoelectric sensor. The final prototype was able to detect vocal vibrations, swallowing, and pulses when placed on the neck and wrist [20]. Although still in research and development, wearable sensors have a variety of applications that can improve medical monitoring and diagnostics.

### 5.2. Implantable Sensors

Recently, the first fully biodegradable piezoelectric sensor was created using poly-L-lactic acid (PLLA) [5]. This technology utilizes the biodegradable, biocompatible, and piezoelectric properties of PLLA nanofibers to create a sensor capable of measuring pressures within the body. This sensor was constructed of layers of PLLA and molybdenum or magnesium between polylactic acid (PLA). Molybdenum and magnesium were selected for their biodegradable properties and previous utilization in FDA-approved implants. The sensor was able to detect pressures ranging from 0 to 18 kPa. The biodegradability of the sensor was also tested with the sensor being fully degraded after 56 days [25].

However, this sensor utilized bulk PLLA and untreated PLLA nanofibers can produce small electrical signals but these electrical signals can become lost in the noise created by the triboelectric effect between other sensor elements. Through an electrospinning process, the reorientation of the PLLA nanofiber's polymer chains increases the molecular dipole moment, resulting in an improved piezoelectric response and signal-to-noise ratio. This treatment improves the alignment of the crystal structure and increases the PLLA nanofiber's crystallinity. The treated PLLA nanofibers exhibit a higher sensitivity to force and were able to sustain their charge output over 10,000 impact cycles [26]. PLLA sensors are a recent technology that shows the most promise for implementation in the medical field. Its progress shows the potential for piezoelectric sensor technologies and prototypes, with different organic materials and combinations, to transform the biomedical wearable and implantable sensor industry.

## 6. Conclusions

Organic piezoelectric biomaterials, including collagen, silk, glycine, and PLLA, are seeing interest in their biomedical applications. There is a specific emphasis on the biocompatible, and biodegradable aspects of the materials being considered. Looking to future research and devices, several obstacles must be considered. Organic materials tend to have weaker piezoelectric responses than their inorganic counterparts [3]. Increasing the piezoelectric effect in organic materials usually comes from an increase in crystallinity which causes a decrease in the desired flexibility of the material [2]. Different combinations of organic materials [9] and processing techniques [26] are being explored to enhance the piezoelectric effect and optimize flexibility and performance. Further investigation into nanostructures or multi-layered structures of the materials could increase the piezoelectric response [3]. Other material factors to consider include the stability and durability of the organic materials, as some organic materials have specific, optimal piezoelectric phases. Additionally, the device design has to factor in the orientation of the piezoelectric effect as some organic materials have shear vs. normal piezoelectricity. The potential usage of high-performance computing and additive manufacturing could further assist with the research and development of organic piezoelectric materials and devices [2]. Although the research into organic piezoelectric materials and sensors is still developing, the continued technological developments will have profound impacts on the biomedical technology and healthcare industry.

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## Conflict of Interest

The author declares no conflict of interest.

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