Engineering Materials

Senentxu Lanceros-Méndez
Carlos M. Costa *Editors*

Piezoelectric Polymers and Polymer Composites for Advanced Applications

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Senentxu Lanceros-Méndez · Carlos M. Costa
Editors

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Editors
Senentxu Lanceros-Méndez
BCMaterials—Basque Center
for Materials, Applications and
Nanostructures
Leioa, Vizcaya, Spain

Carlos M. Costa
University of Minho
Braga, Portugal

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Preface and Acknowledgements

> *New material demands new methods, and new methods fling a challenge to old convention.*
>
> *—Lawren Harris (1885–1970)*

Taking into account the Internet of Things (IoT) and Industry 4.0 paradigms and their demand of smart and multifunctional materials, piezoelectric polymers and composites are receiving increasing attention, as they can be applied in a wide range of applications from electronics to biomedical applications, from sensors and actuators to energy generation and storage.

In this book, the current state of the art on piezoelectric polymers in single state, composites and blends, their preparation and characterization are described, together with their main applications. The book emphasizes recent advances in various piezoelectric polymers, focussing also on their technological applications.

The main constituents and applications for piezoelectric composites that are now under development are discussed, along with the advantages, challenges and most recent developments in this field of research.

Piezoelectric polymers and polymer composites and blends are a current and timely research and technological field. Thus, it is timely and relevant book in the field, that summarizes current knowledge and sets the main research directions in the different materials, processing and application areas.

The first chapter "Piezoelectric Polymers and Polymer Composites" presents an overview on piezoelectric polymers and composites, including a description of the concept of piezoelectricity and the main characteristics of the materials. Furthermore, some aspects of the circular economy paradigm are described.

The second chapter "Synthetic Piezoelectric Polymers" focusses on the characteristics of the most relevant and commonly used synthetic piezoelectric polymers.

The third chapter "Organic and Biological Piezoelectric Materials" is dedicated to organic and biological piezoelectric materials where the main piezoelectric properties of these materials are present.

Chapters "Fundamentals of Piezoelectric Poly(L-lactide): Chain Morphology, Characterization, and Processing" and "Piezoelectric Characterization of the Shear Piezoelectric Poly(L-lactide)" are about the piezoelectric polymer poly(L lactide), PLLA, focussing on the piezoelectric chain morphology and the different processing strategies to obtain it. Furthermore, the characterization and activation of the piezoelectric response are presented.

The sixth chapter "Piezoelectric Polymer Composites" describes the most studied and applied piezoelectric polymer composites, with particular attention to poly(vinylidene fluoride), PVDF, based piezoelectric composites and their corresponding applications.

The seventh chapter "Piezoelectric Polymer Blends Interfacing Biomedical Technologies" focusses on piezoelectric polymer blends and their implementation in the biomedical field.

The eighth chapter "Application of Piezoelectric Polymers in Additive Manufacturing" presents the processability of piezoelectric polymers through additive manufacturing, by different processing techniques.

The ninth chapter "Piezoelectric Sensors and Actuators for Electronic Applications" provides an overview of the applicability of piezoelectric polymers and polymer composites for sensors and actuators, describing the working/operating principles, fabrication procedures, structure of the devices and performance in specific applications.

The tenth chapter "Piezoelectric Polymer Nanocomposites for Energy Storage and Harvesting Applications" describes the implementation of polymer nanocomposites in energy storage and harvesting, demonstrating the main advantages of these materials over traditional inorganic composites.

The eleventh chapter "Fascinating PVDF for Harvesting Applications" deals with the application of poly(vinylidene fluoride) and its copolymers for energy harvesting applications.

The twelfth chapter "Electrocaloric Polymers and Related Materials" describes the electrocaloric effect (ECE) and the materials and devices advancing electrocaloric (EC) cooling technology.

Chapters "Hydrogel-Based Piezoelectric Film Devices for Biomedical Applications" and "Piezoelectric Polymers for Tissue Engineering and Regeneration" are devoted to the biomedical applications of organic and biological piezoelectric materials, to hydrogel-based piezoelectric materials and to piezoelectric materials for tissue regeneration, respectively.

In the scope of environmental applications, the fifteenth chapter "Poly(Vinylidene Fluoride)-Based Membranes for Water Remediation" focusses on poly(vinylidene fluoride) based membranes for water remediation applications, describing different remediation strategies based on a variety of composite membranes and remediation principles.

Finally, the sixteenth chapter "Challenges and Outlook" represents an overview of these piezoelectric polymer-based materials, highlighting the main needs and future trends.

Due to the diversity of materials and applications, this book would not have been possible without the outstanding contributions, commitment and dedication of the authors who accepted the request to write the corresponding chapters. The editors truly and warmly thank the time and work invested in writing these chapters, which will serve as a state-of-the-art reference and as a roadmap for future advancements in this field. We are honoured and truly enjoyed and felt privileged to have contacted and collaborated with you to achieve the significant accomplishment that this book signifies!

Furthermore, this book would not have been possible without the cooperation, comprehension and commitment of our research groups at the University of Minho in Braga, Portugal, and BCMaterials, the Basque Center for Materials, Applications, and Nanostructures in Leioa, Spain. Advancing science and technology via the conceptualization, composition and production of a book is among the most comprehensive and pertinent endeavours we can provide to you all!

Finally, but no less relevant, we sincerely appreciate the outstanding assistance provided by the Springer team, starting with the initial conversations with Mayra Castro and Martina Wiese and continuing with the dedicated, kind and efficient support from Ashok Arumairaj. This book would not have been possible without their unwavering support, technical know-how, tolerance and kindness. We have enjoyed working with each and every one of you!

The book provides a comprehensive state of the art of piezoelectric polymers and composites, their scientific and technological advances. This family of materials will continue to play a central and increasing role in the rapid technological developments we are experiencing, aiming at a more interconnected, efficient, sustainable and just society. We are convinced that this book will become a milestone to further promote scientific and engineering advances and to support the achievements of those high-level objectives we all aim contributing to.

Braga, Portugal
Leioa, Spain

Carlos M. Costa
Senentxu Lanceros-Méndez

Contents

Piezoelectric Polymers and Polymer Composites

L. Fernandes, Harvey Amorín, Cristina Pascual-González, Miguel Algueró, C. M. Costa, and S. Lanceros-Méndez

Abstract Materials with the capacity to transform mechanical stresses into electrical energy and vice versa include piezoelectric polymers and polymer composites. The chapter introduces the piezoelectric effect and discusses polymer composites, emphasizing the polymer matrix and fillers to enhance performance and tune specific materials characteristics. We illustrate the versatility of these materials by analyzing the impact of filler type, size, and distribution on the composite's piezoelectric response and its potential applications in biomedical devices, sensors, actuators, and energy harvesting. Lastly, we discuss present issues and needed advancements, such as the development of eco-friendly piezoelectric polymers and composites, which will further promote technological development and implementation.

Keywords Composites · Piezoelectric polymers · Fillers · Advanced applications

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L. Fernandes · C. M. Costa (✉) · S. Lanceros-Méndez
Physics Centre of Minho and Porto Universities (CF-UM-UP) and Laboratory of Physics for Materials and Emergent Technologies, LapMET, University of Minho, Braga, Portugal
e-mail: cmscosta@fisica.uminho.pt

H. Amorín · C. Pascual-González · M. Algueró
Instituto de Ciencia de Materiales de Madrid, CSIC, Madrid, Spain

C. M. Costa
Institute of Science and Innovation for Bio-Sustainability (IB-S), University of Minho, Braga, Portugal

S. Lanceros-Méndez
BCMaterials, Basque Center for Materials, Applications and Nanostructures, Leioa, Spain

Ikerbasque, Basque Foundation for Science, Bilbao, Spain

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1 Introduction

The concept of piezoelectricity first appeared in the late 19th century and has been gathering an increasing attention since [1]. Presently, with the concepts of the Internet of Things (IoT) and next *Industry 5.0*, which demand smart and multifunctional materials, piezoelectric materials are on the radar for implementation in advanced applications [2]. Piezoelectricity refers to the ability of certain materials to generate an electrical response, related to asymmetric displacements of charges, when subjected to mechanical stress, and also linearly deform under the application of an electric field [2]. As such, piezoelectric materials have been extensively used for actuation and sensing [3], and are a key enabling technology for the next generation of smart and flexible devices, with great prospective in energy harvesting and biomedical fields [3–6]. These materials are able to capture and convert ambient mechanical vibrations into electrical energy, to autonomously power, for instance, wireless sensor networks (WSNs) and develop self-powered systems.

Most of the state-of-the-art piezoelectric materials are ceramics, a mature and ubiquitous technology for electromechanical transduction. However, they are brittle and stiff and cannot satisfy the increasing demand of flexible smart devices. This is the case of wearable sensors and actuators for smart clothing or in medical diagnosis/therapy, and also of bio-implanted medical devices, where autonomous powering is highly desirable [7]. Among alternative materials, polymers have been also implemented in a variety of applications. Despite they lower piezoelectric response, they present clear advantages against ceramics, which are relevant in different application areas, such as easy of molding, flexibility and lightweight, which in turn translates into a low-cost fabrication with high throughput [8]. In addition, polymers also show small acoustical impedance, comparable to that of water, that strongly facilitates power transmission with living tissue [9]. Organic materials like collagen, keratin, silk and even DNA also exhibit piezoelectric properties.

An approach capable of enhancing the piezoelectric response of polymer materials, while preserving flexibility and mechanical performance, is the use of polymer composites [6]. These materials rely on the combination of a flexible polymeric matrix with one or more complementary fillers that can improve the polymer properties (such as thermal and mechanical properties) or provide or optimize a functional response. In the fabrication of these composites, the manufacturing and dispersion methods, as well as the filler shape and size are key factors in properly tunning their properties [10]. Among the several filler types (namely, magnetic, conductive, or ceramic), ceramic fillers have been extensively used in this field, in particular those with low dielectric and mechanical losses, wide range of dielectric constants and high piezoelectric coefficients [10, 11]. Furthermore, among the different possible connectivity schemes, most attractive configurations compatible with additive processing technologies are the one consisting on ceramic fillers dispersed into a polymer matrix and laminate structures [12]. The arrangement of composite components is described by its connectivity, determining how the various phases of the composite materials interconnect with each other. This connectivity plays a pivotal role in shaping the ultimate structure and functional response of composites in general and, in particular, of piezoelectric polymer composites, also influencing their potential applications [13].

A contemporary trend in the realm of piezoelectric composites involves fabricating these materials with dual fillers. Examples include combinations of ceramic and conductive fillers, ceramic and magnetic fillers, and compositions like core–shell structures [14–16]. This approach aims to enhance performance and introduce multifunctionality, particularly for applications in areas such as dielectric-based capacitors, batteries, electronic devices, magnetoelectric transduction and microwave absorption devices.

Last but not least, the principles of reutilization, recycling, and reduction, fostering a circular economy and sustainability, have demonstrated significant influence on the socio-economic paradigm, yielding substantial benefits [17]. Piezoelectric composites are not oblivious to this trend, with growing attention directed towards their recyclability and/or reusability, along with a focus on exploring more natural/sustainable sources for material development [18]. As such, some aspects of piezoelectric composites that need to be considered regarding the circular economy paradigm are:

1. *Circular design principles*: Entailing developing products and materials that facilitate easy disassembly, repair, and recycling. This strategy aims to optimize resource efficiency and diminish environmental impact [19].
2. *Life cycle assessment (LCA)*: Assessing the environmental effects across their entire life cycle is critical to comprehend their role in sustainability. This involves evaluating the extraction of raw materials, manufacturing processes, product usage, and considerations for end-of-life disposal [19].
3. *Material selection*: Selecting materials with minimal environmental impact and verifying their sustainable sourcing is a critical aspect. This involves investigating natural and sustainable sources for the polymer and fillers, decreasing reliance on limited resources, and favoring environmentally friendly alternatives [18].
4. *End-of-life considerations*: Recognizing the environmental consequences and disposal complexities associated with composites is essential to develop materials with straightforward disassembly or recycling procedures that not only lessens the environmental impact but aligns with the principles of a circular economy [19].
5. *Extended product life*: Improving the durability and lifespan of composites also plays an important role in a circular economy paradigm by lessening the need for frequent replacements and decreasing waste generation [20].
6. *Recyclability and reusability*: Examining the components involved in composites development, including polymer and filler, regarding their potential for recycling and reusability. Crafting composites with elements that can be easily separated and repurposed plays an increasing role in circular and sustainable economy [21].

To sum up, the circular economy paradigm promotes a transition from a linear "take-make-dispose" model to a more sustainable and regenerative approach. Integrating these principles into the production, use, and disposal of piezoelectric composites can foster a technology landscape that is environmentally friendly and socially responsible [17].

2 Definition and Basic Concepts

The term “piezoelectricity” was coined by Hankel in 1881 and means “electricity by pressure”, stemming from the Greek word “piezo” meaning pressure [1]. However, the concept itself was uncovered a year earlier, in 1880, by Pierre and Jacques Curie [22], who observed the generation of electricity in certain crystals such as quartz (SiO_2) when subjected to a mechanical stress (direct piezoelectric effect). Shortly after, the converse piezoelectric effect was predicted by Lippmann in 1881, based on thermodynamic theory [23]. The direct and converse piezoelectric effects are presented in Fig. 1 [24, 25].

The piezoelectric effect involves the conversion of mechanical energy into electrical one, and vice versa, where the symmetry of the crystal structure plays a fundamental role. In other words, this phenomenon only occurs in crystalline non-centrosymmetric materials, meaning they lack a center of symmetry in their crystal lattice, providing unique insights into the physics of solid state and serving as a valuable testing ground for theoretical and computational predictions. Finally, in a publication in 1919 by Woldemar Voigt, the 20 natural crystal classes exhibiting piezoelectricity were outlined, also defining the piezoelectric constants through tensor analysis [26].

Materials exhibiting this property show induced or change of polarization when a stress field is applied, due to displacement of positive and negative charges within the material, thus generating an external electric potential. Conversely, when an electric field is applied, dipole moments (or charges) are subjected to forces that cause them to reorient (or separates) leading to distortion of crystal lattice and changes in material’s dimensions, such as expansion or contraction. The piezoelectric effect is reversible, so when stimulus is removed the material returns to its original state, either of polarization or strain.

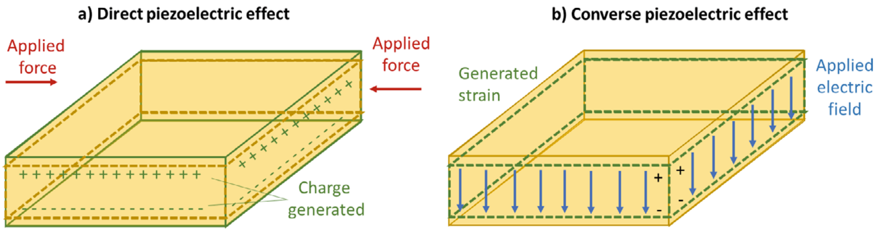

Fig. 1 Direct and converse piezoelectric effects

Since the Curie brothers demonstrated piezoelectric effects in various crystals in 1880, the field has significantly advanced, particularly in sensor and actuator applications [24, 27]. However, a significant breakthrough occurred in 1969 when Kawai discovered a robust piezoelectric effect in the polymer poly (vinylidene fluoride) (PVDF), introducing mechanically flexible materials to the realm of piezoelectricity [28], and expanding the range of applications to include flexible electronics, large-area sensors, flexible energy harvesters, and biomedical devices, by exploiting, in one way or another, the coupling of mechanical and electrical parameters [29].

Both the direct and indirect piezoelectric effects can be represented by a pair of linear constitutive strain-charge equations [30, 31]:

$$S_p = s_{pq}^{E} T_q + d_{pk} E_k \tag{1}$$

$$D_i = d_{iq} T_q + \varepsilon_{ik}^{T} E_k \tag{2}$$

where T is the mechanical stress, S the strain, D the electric displacement, and E the electric field strength; whereas s_{pq}^{E} is the elastic compliance tensor, d_{iq} the piezoelectric constant tensor, and ε_{ik}^{T} the dielectric constant tensor. Symmetry considerations allow the Voigt notation to be used, so that independent variables relative to stress can be labelled as illustrated in Fig. 2, to allow the indices to be contracted. Schematically, indices 4, 5 and 6 are considered as rotations about the axes 1, 2 and 3, respectively [32]. In single crystals, these indices refer to directions of the crystalline unit cell (Cartesian coordinate axes x, y, and z), where polarization orientation is usually taken along the z-axis, whereas for semi-crystalline polymers, as well as polymer composites, indices may correspond to other orientations such as stretch direction or molecular chain orientation.

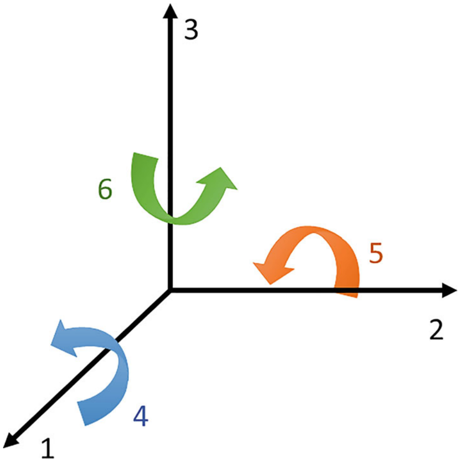

Fig. 2 Schematic representation of the directions referred to the voigt notation [29]

For example, in the context of piezo-/ferroelectric polymers like PVDF, axis 1 typically aligns with the draw or stretch direction, axis 2 corresponds to the transverse direction, and axis 3 represents the thickness or polarization axis [33]. Applying this correlation in Eqs. 1 and 2 yields the following expressions:

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix} = \begin{bmatrix} s_{11}^E & s_{12}^E & s_{13}^E & s_{14}^E & s_{15}^E & s_{16}^E \\ s_{21}^E & s_{22}^E & s_{23}^E & s_{24}^E & s_{25}^E & s_{26}^E \\ s_{31}^E & s_{32}^E & s_{33}^E & s_{34}^E & s_{35}^E & s_{36}^E \\ s_{41}^E & s_{42}^E & s_{43}^E & s_{44}^E & s_{45}^E & s_{46}^E \\ s_{51}^E & s_{52}^E & s_{53}^E & s_{54}^E & s_{55}^E & s_{56}^E \\ s_{61}^E & s_{62}^E & s_{63}^E & s_{64}^E & s_{65}^E & s_{66}^E \end{bmatrix} \begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} + \begin{bmatrix} d_{11} & d_{12} & d_{13} \\ d_{21} & d_{22} & d_{23} \\ d_{31} & d_{32} & d_{33} \\ d_{41} & d_{42} & d_{43} \\ d_{51} & d_{52} & d_{53} \\ d_{61} & d_{62} & d_{63} \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \tag{3}$$

$$\begin{bmatrix} D_1 \\ D_2 \\ D_3 \end{bmatrix} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} + \begin{bmatrix} \varepsilon_{11}^T & \varepsilon_{12}^T & \varepsilon_{13}^T \\ \varepsilon_{21}^T & \varepsilon_{22}^T & \varepsilon_{23}^T \\ \varepsilon_{31}^T & \varepsilon_{32}^T & \varepsilon_{33}^T \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \tag{4}$$

According to Eqs. 1 and 2, there are 18 potential ways to interconnect the electrical and mechanical parameters of a piezoelectric material, with each configuration falling into one of four distinct operating modes [27]. These primary operating modes are denoted as longitudinal (L), longitudinal shear ($\mathrm{S_L}$), transverse (T), and transverse shear ($\mathrm{S_T}$), as illustrated in Fig. 3 [34].

Considering the direct piezoelectric effect, the application of mechanical stress results in an electric flux density and consequently induces a macroscopic variation in the material's polarization in a specific direction [34]. The corresponding operating modes and the equivalent polarization variations are detailed in Table 1.

Processing conditions and the specific crystal structure of piezoelectric materials dictate which elements of the dielectric constant, piezoelectric, and elastic compliance tensors are non-zero and distinctive. For instance, in the case of an unstretched and poled piezoelectric poly (vinylidene fluoride trifluoroethylene) (P(VDF-TrFE))

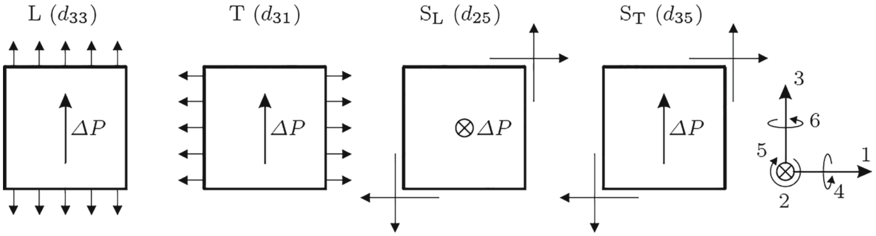

Fig. 3 Diagram depicting the four operational modes of the piezoelectric effect. ΔP represents the macroscopic alteration in electric polarization [34]

Table 1 Modes of direct piezoelectric operation with concise descriptions [27]

Operating mode	Denomination	Description
Longitudinal mode (L)	d_{11}, d_{22} and d_{33}	Application of a normal stress coinciding with change in the direction of electric polarization
Transverse mode (T)	d_{12}, d_{13}, d_{21}, d_{23}, d_{31} and d_{32}	Alteration in electric polarization perpendicular to the mechanical load
Longitudinal shear mode (S_L)	d_{14}, d_{25} and d_{36}	Application of shear stress coupled with a change in electric polarization perpendicular to the plane of the shearing stress
Transverse shear mode (S_T)	d_{15}, d_{16}, d_{24}, d_{26}, d_{34} and d_{35}	Alteration in electric polarization within the plane of the shearing stress

copolymer with a macroscopic symmetry of 2 *mm* (*e.g.* analogous to 4 *mm* of $BaTiO_3$), the matrix form of Eqs. 3 and 4 can be expressed as [25, 30]:

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix} = \begin{bmatrix} s_{11}^E & s_{12}^E & s_{13}^E & 0 & 0 & 0 \\ s_{21}^E & s_{22}^E & s_{23}^E & 0 & 0 & 0 \\ s_{31}^E & s_{32}^E & s_{33}^E & 0 & 0 & 0 \\ 0 & 0 & 0 & s_{44}^E & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{55}^E & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{66}^E \end{bmatrix} \begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} + \begin{bmatrix} 0 & 0 & d_{13} \\ 0 & 0 & d_{23} \\ 0 & 0 & d_{33} \\ 0 & d_{24} & 0 \\ d_{15} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \tag{5}$$

$$\begin{bmatrix} D_1 \\ D_2 \\ D_3 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} + \begin{bmatrix} \varepsilon_{11}^T & 0 & 0 \\ 0 & \varepsilon_{22}^T & 0 \\ 0 & 0 & \varepsilon_{33}^T \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \tag{6}$$

Piezoelectric materials belong to the class of dielectric materials, encompassing both inorganic and organic phases, whose polarization can be altered by the application of mechanical stress or vice versa. These materials can be categorized into two classes: polar and non-polar piezoelectric materials, depending on the presence of a permanent dipole moment or a null total dipole moment, respectively [31]. Naturally non-polar piezoelectric materials, like quartz and berlinite, lack a center of symmetry in their crystalline structure, rendering them inherently piezoelectrics. In contrast, engineered materials such as barium titanate ($BaTiO_3$, BTO) and lead zirconate titanate ($Pb(Zr,Ti)O_3$, PZT) typically need to undergo a poling process to exhibit macroscopic piezoelectricity. Among polar synthetic crystals, perovskite

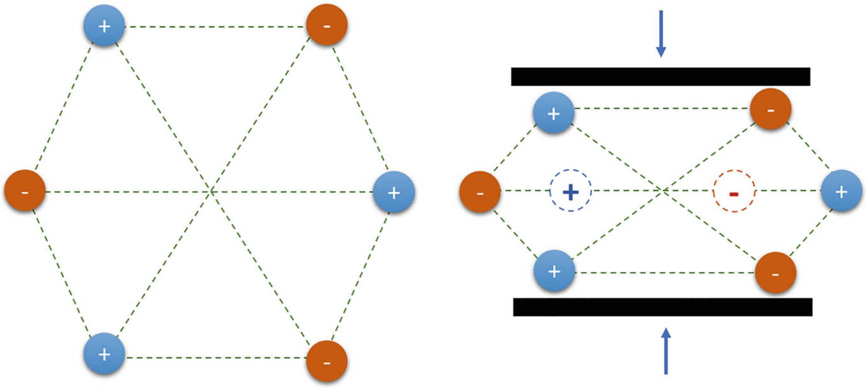

Fig. 4 Schematic diagram of piezoelectricity in a system under a compressive force

materials, with the general formula ABX_3, demonstrate effectiveness in being poled to enhance their piezoelectric properties [35].

From the beginning, it was understood that the piezoelectric effect is intrinsically linked to the symmetry of the crystal structure. Indeed, piezoelectric effect is prominent when the crystals are cut in specific directions, so that different cuts reveal different atomic arrangements that determine how the crystals deform and generate electrical charges under stress, or deform when subjected to an electric field. The relationship between crystallinity and piezoelectricity is visualized in Fig. 4, where the centers of negative and positive charges coincide, resulting in a neutral system. However, under compressive forces, these centers for negative and positive charges separate, creating a dipole. This separation is responsible for generating an electric field in piezoelectric materials when subjected to pressure or deformation [36].

Among piezoelectric materials, some possess a unique polar axis whose orientation can be switched by an external electric field; these are called ferroelectrics. They offers clear advantages when used as piezoelectrics, not only because of their higher piezoelectric coefficients, strong electromechanical coupling and large strain responses, but also they offer great versatility thanks to the ability to engineer domains, adjust composition, apply strain engineering, or maximize the piezoelectric response by operating near the Curie temperature, where the material transits from the polar state to the non-polar one, and piezoelectric coefficients increase drastically.

In ferroelectric materials, dipoles typically exhibit random orientations, leading to any distinct macroscopic piezoelectric effect [37]. These materials can be brought into a single polar state (or domain orientation) by applying an external electric field. This process is known as poling, where the application of a strong electric field, surpassing the saturation field but remaining below the electrical breakdown, induces alignment of polar domains. This is typically done at elevated temperatures to enhance domain mobility and/or dipole reorientation, while still being maintained below the Curie temperature [38]. To sustain this effect, the material is subsequently cooled in the presence of the high electric field [36]. Once the material is

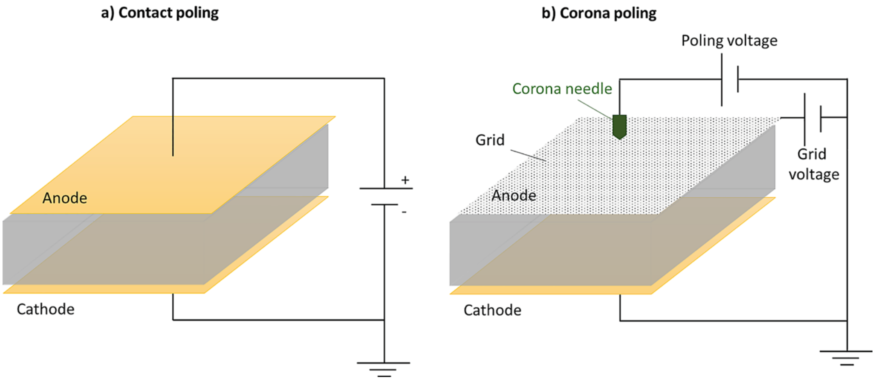

Fig. 5 Poling systems **a** contact poling and **b** corona poling

poled, the previously random or misaligned dipoles become aligned, leading to a net macroscopic polarization and enabling piezoelectric behavior.

Two widely adopted poling methods are contact poling and corona poling (Fig. 5). The former is typically used in polycrystalline ferroelectric ceramics and the latter is often applied to polymeric materials. In contact poling, the material is positioned between two electrodes and subjected to a high voltage [39]. On the other hand, corona poling involves connecting only one side of the material to an electrode, leaving the opposite surface free. A sharp corona tip, held at a high voltage in the kilovolt range, hovers just above the free surface, while the material itself is supplied with a low voltage through the electrode. The highly charged tip ionizes surrounding gas molecules, causing them to accelerate towards and deposit onto the material's free surface, thereby poling the material [36].

Summarizing, piezoelectricity refers to the ability of certain materials to generate surface charges in response to applied mechanical stress, known as the direct piezoelectric effect. Conversely, these materials also undergo mechanical strain when subjected to an applied electric field, termed the converse piezoelectric effect [25]. This phenomenon manifests in materials characterized by a non-centrosymmetric crystal structure (though there are also amorphous polymers showing this effect).

3 Piezoelectricity in Ceramics and Polymers

Piezoelectric parameters, figures of merit (FOMs), serve as valuable means to assess and compare the properties of piezoelectric materials, to properly select materials and to design applications. Most relevant FOMs are the piezoelectric charge/strain coefficient, piezoelectric voltage coefficient, and the electromechanical coupling factor. Other parameters can also be of relevance and even determinant for a specific application, such as the mechanical coupling factor and acoustic impedance, as well as intrinsic materials parameters, such as the Curie temperature, or Young's modulus, among others [40].

The piezoelectric charge/strain constant, denoted as d, and already mentioned, represents the relationship between the induced charge density (x) caused by an applied mechanical stress (σ) (Eq. 7). Alternatively, d can also be expressed as the correlation between the strain (ε) generated when an external electric field (E) is applied [36]:

$$d = \frac{x}{\sigma} = \frac{\varepsilon}{E} \tag{7}$$

The piezoelectric voltage constant (an important FOM in sensor applications), denoted as g, establish the relationship between the induced electric field (E) and the external applied stress (σ) (Eq. 8). This relationship is linked to the piezoelectric charge coefficient through the Legendre transformation and lacks a straightforward inverse correlation [40].

$$g = \frac{E}{\sigma} \tag{8}$$

Combining these two equations, an important relation between g and d is obtained:

$$g = \frac{d}{\varepsilon_0 \varepsilon} \tag{9}$$

where ε is the relative permittivity. The electromechanical coupling factor, denoted as k^2, is characterized by the ratio of input and stored energies, encompassing both the direct and reverse piezoelectric effects. The equations governing this FOM are presented in Eqs. 10 [25]:

$$k^2 = \frac{\textit{stored mechanical energy}}{\textit{input electrical energy}} = \frac{\textit{stored electrical energy}}{\textit{input mechanical energy}} \tag{10}$$

In polymer materials, and in particular in PVDF, there are two main piezoelectric modes, as shown in Fig. 6. The first is d_{33}, also called the longitudinal mode, where the direction of polarization is parallel to the direction of stress. The second is d_{31}, known as the transverse mode, where the polarization direction is perpendicular to the applied stress direction [37]. Generally, the value of d_{33} is higher than d_{31}, thus generating a larger voltage output under compressing or stretching. This makes the d_{33} mode more favorable for various applications, the specific application defining, in any case, which is the required geometry and, therefore the specific mode [41]. Besides, despite the typically low piezoelectric charge coefficients as compared to ceramics, polymers have very low dielectric permittivity that leads to very high piezoelectric voltage coefficients, a key figure of merit for sensor applications.

Piezoelectricity occurs in a range of inorganic materials, such as natural quartz (SiO_2) that show small d_{11} piezoelectric coefficient (2 pC/N), and a number of

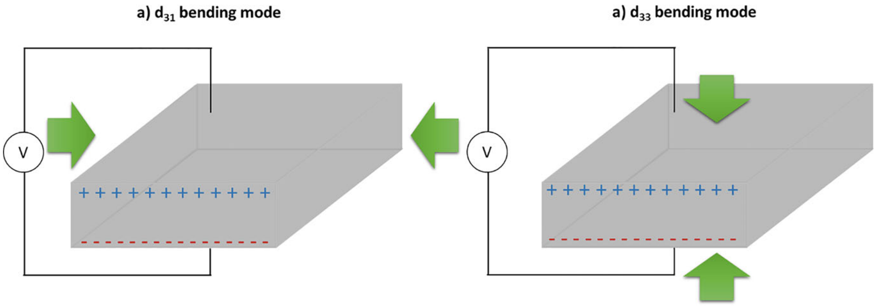

Fig. 6 Main modes for piezoelectric materials: **a** d_{31} and **b** d_{33} modes

synthetic crystals like $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZN–PT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT), which present ultra-high piezoelectric coefficients $d_{33} > 2500$ pC/N, electromechanical coupling factors ($k_{33} > 94\%$), high sensitivity and strain energy density, but their fragility is often a significant limitation, especially in high-stress applications [42]. Polycrystalline ceramics show piezoelectric properties 100 times greater than quartz, for instance, but they are not natural piezoelectrics and need to be poled under a high voltage to show piezoelectricity. Piezoelectric ceramics offer numerous advantages, including cost-effectiveness, stability, straightforward fabrication techniques, and the versatility to be shaped into various forms. Consequently, they have found widespread use in diverse applications owing to their superior piezoelectric performance, such as transducers, sensors, and actuators [36].

High-sensitivity piezoelectrics are mostly perovskite oxides, and current state-of-the-art material is $Pb(Zr,Ti)O_3$ (d_{33} above 600 pC/N) at the morphotropic phase boundary (MPB) between ferroelectric polymorphs [43]. The domain dynamics also play a major role, and large piezoelectric coefficients can be achieved by enhancing the ferroelectric/ferroelastic domain walls mobility [44]. However, piezoelectric ceramics are often composed of lead-containing compounds [40], and a main line of research at the cutting edge of the field is the search of novel perovskite systems that can replace PZT, while being environmentally friendly to comply with enforced environmental regulations that require the elimination of lead from electronic equipment [45]. Besides, health concerns related to lead toxicity hinder their potential use as active biomedical implants, where piezoelectric materials can interact with bones and cells through electrical signals.

The development of lead-free alternatives like $BaTiO_3$-based and alkaline niobite systems (KNN or $K_{0.5}Na_{0.5}NbO_3$) has gained prominence. An alternative was thought to have been found in 2004, when piezoelectric coefficients above 300 pC/N were reported for a KNN-based composition, which increased above 400 pC/N by ceramic texturing [46]. Although mechanism entails large temperature dependences that limit performance. More recently, Ca and Zr co-doped $BaTiO_3$ has emerged as lead-free leading candidate owing to reported high piezoelectric coefficients (d_{33} above 620 pC/N), though its low Curie point could be a limitation in many application [47].

Besides, ceramic processing is still challenging and requires very high temperatures that normally results in abnormal grain growth and brittle microstructures that compromise reliability [48]. Special attention has also been paid to Bi-containing perovskites, attending to the presence of lone-pair cations at the perovskite A-site, considered essential for high piezoelectric sensitivity, yet advances are hindered by thermodynamic instability associated with a low tolerance factor [49].

On the other hand, polymers were traditionally not associated with piezoelectricity until the late 1960s when Kawai et al. [28] discovered their potential for practical applications. For polymers to exhibit piezoelectric properties, they must contain molecular dipoles and the ability to orient them under strain or electric fields (poling). There are two main types of piezoelectric polymers: semi-crystalline, exemplified by PVDF and its copolymers that display the highest piezoelectric coefficients among all thermoplastic polymers ($d_{33} > 30$ pC/N and d_{31} of 25 pC/N), and amorphous. The former feature small ferroelectric crystals within an amorphous matrix, achieving pronounced macroscopic piezoelectric response upon poling. In contrast, amorphous polymers possess dipoles but lack long-range order, maintaining a quasi-stable state after poling [37].

Alternatively, and among semi-crystalline, optically active polymers such as polylactides (PLA), are of growing interest, not only due to their origin from renewable sources and biodegradation, but also because they can be piezoelectric without need of a high-voltage poling process [50]. Piezoelectricity of PLA is radically different from that of PVDF [51]. It is non-ferroelectric (the organic analog to quartz), yet only exhibits shear piezoelectric coefficients (d_{14} and d_{25}), so that a macroscopic polarization is only achieved with the application of shear stress/strain along a specific direction regarding the molecular chain.

Piezoelectric coefficients $d_{14} > 10$ pC/N have been reported for uniaxially stretched poly-L-lactide, which results in huge shear piezoelectric voltage coefficients, $g_{14} > 0.5$ V·m/N, due to the very low dielectric permittivity of this polymer [32].

4 Piezoelectric Composites Materials

Smart polymer-based composite materials have concentrated increasing attention in the last decades, among which piezoelectric composites are considered very promising for enhancing piezoelectric charge response, while maintaining low permittivity for a high voltage output, preserving flexibility and mechanical performance [8]. The properties of these materials, as well as their processability and integration into devices, can be fine-tuned by adjusting factors like the proportion of constituent materials, their connectivity, and overall structure [27]. For instance, piezoelectric polymers, while typically show low piezoelectric coefficients, also exhibit good acoustic impedance matching with common materials like living tissue and water. Conversely, ceramic piezoelectric materials boast high piezoelectric coefficients but do not acoustically match well with the aforementioned media. A composite comprising both polymer and ceramic piezoelectric components can yield a material with a balanced combination of excellent piezoelectric performance and suitable compatibility, allowing for customization to meet the specific requirements of the targeted application [36]. Most topical smart hybrid composites are piezoelectric ones, and commercial products are already available, like ultrasound transducers, combining the ceramic high piezoelectric coefficients with the polymer low acoustic impedance [52]. These composites consist of piezoceramic columns embedded in a polymeric matrix, fabricated by either cost and time inefficient dice and fill procedures (a subtractive manufacturing that entails large amounts of waste material), or arrange and fill methods that do not provide enough accurate microstructural control.

The choice of piezoelectric materials for specific applications depends on their individual strengths and weaknesses (Fig. 7). Ceramic piezoelectric materials, suitable for micro-electromechanical systems (MEMS) devices and transducers like sonar technology, provide a robust piezoelectric response but lack flexibility. Piezoelectric polymers excel in flexible applications such as wearable electronic fabrics for sensing and energy harvesting, as well as in biomedical applications like self-powered implants and bone tissue scaffolding due to their compatibility with the human body, being also processable by additive manufacturing. Composite materials, the most versatile among piezoelectric materials, find applications in diverse fields including tactile sensors, soft robotics, energy harvesting and biomedical applications [27, 36].

The achievement of superior properties in piezoelectric composites is the result of the synergistic combination of the constituent phases [13]. This has led to a growing demand for such composites, offering a common approach to customizing material properties for specific applications. The configuration of the phases within the composite significantly influences its electromechanical coupling. The concept of connectivity, introduced by Newnham et al. [53] in the late 1970s, has driven research on piezoelectric composites. Diverse connectivities, such as 0–3, 1–3, 2–2, and 3–3

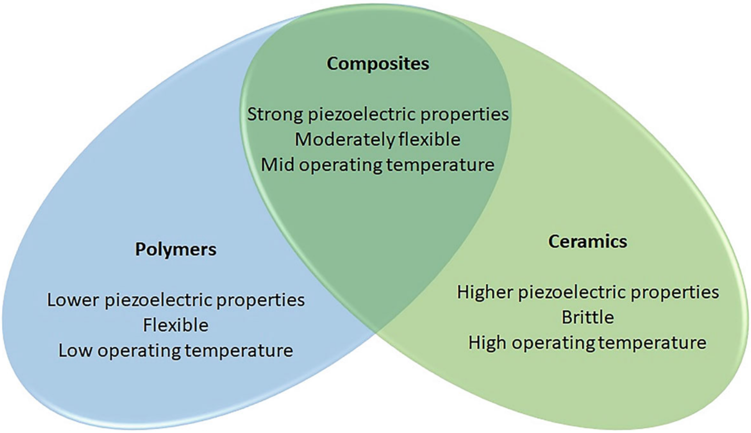

Fig. 7 Comparison of relevant characteristics of polymeric and ceramic piezoelectric materials

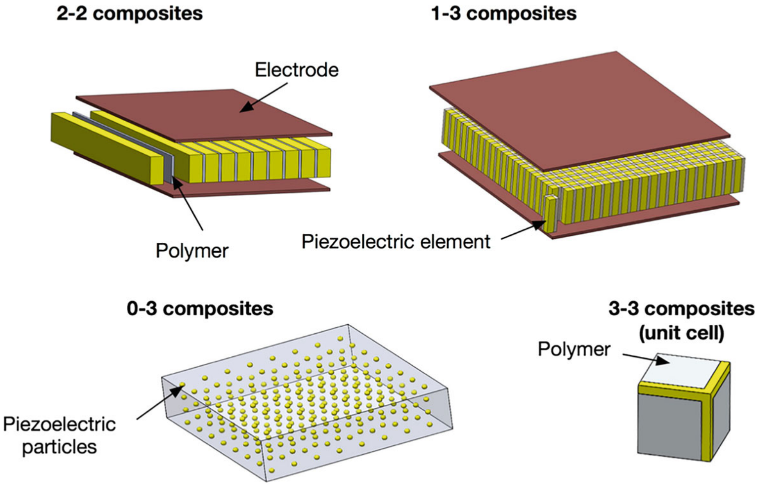

Fig. 8 Schematic representation of most common piezoelectric composites and their corresponding connectivity [55]

configurations, have been explored for piezoelectric composites (Fig. 8). Among the various connectivities, the 0–3 and 2–2 patterns have garnered the most attention, where the first number refers to physical connectivity of the active phase (ceramic filler) and the second number to the polymer phase [3, 54]. The most attractive configuration compatible with additive processing technologies is the 0–3 connectivity that consists of piezoelectric ceramic fillers embedded into a polymer matrix, which is three-dimensionally connected and in turn can also be piezoelectric. A major issue in this configuration is the inhomogeneous dispersion and agglomeration of the particles within the matrix when prepared by conventional processing techniques, and to poor bonding between components. This hinders efficient ferroelectric poling, required for having macroscopic piezoelectric effect.

Additionally, these composites may include other fillers, such as conductive and magnetic fillers, with the former being added in small quantities to prevent exceeding the threshold of high conductivity [55]. For instance, magnetoelectric polymer composites consisting of magnetostrictive metallic particles embedded in piezoelectric polymeric matrices [56].

Various combinations and arrangements between fillers and polymer components have been proposed in the development of piezoelectric composites, where phase connectivity significantly influences the ultimate composite properties. Laminated composites (2–2 connectivity), organized in layered structures, are also prevalent in literature and applications. Poling is largely facilitated in these layered structures, which are less prone to dielectric breakdown when using conductive fillers. Indeed, this is why laminate composites systematically provide larger responses than particulate ones, and why most work has been focused on this configuration even if modelling indicates that similar responses can be attained with particulate systems. A main issue in all cases is the compatibility between components, along with the elastic coupling across interfaces. A more detailed summary of the main characteristics of piezoelectric composite regarding their connectivities is shown in Table 2.

It is widely reckoned that interfaces and the nature and intensity of interactions between ceramic particles and polymeric matrix play also a key role in the composite performance. For instance, in PVDF-based polymers the crystallization behavior strongly depends on these interfacial interactions, so that the fraction of β phase is generally increased by the presence of particles depending also on the surface characteristics [57]. Agglomeration of the ceramic particles, or presence of pores and voids at interfaces are factors that limit composite performance and are thought to often be behind the lack of reproducibility in properties reported so far in literature. Chemical surface modifiers, such as surfactants or silane agents are commonly used to address these issues. Interfaces also play a major role in composite performance. For instance, interfacial polarization can appear giving additional contributions to the overall dielectric permittivity. Also, unbonded molecular species provide conduction paths that increase losses and reduce dielectric strength. All these aspects affect poling, which in turn determines the piezoelectric performance.

Summarizing, polymer composites should offer attributes like low density, flexibility, notable mechanical properties, thermal stability, and elevated dielectric and piezoelectric coefficients, as compared to the piezoelectric polymers [27]. Some common piezoelectric composites used nowadays are for example PVDF/PZT, PVDF/$BaTiO_3$ and PVDF/ZnO, among others [36]. In the following sections, a more in-depth overview of the properties of some of the most common polymers and fillers used in the design of piezoelectric polymer composites is provided.

Table 2 Relevant characteristics of piezoelectric composites, depending on their connectivity [25, 55]

Connectivity	Advantages
0–3	• Excellent flexibility • Elevated piezoelectric voltage • Capability for intricate shapes and printability
3–3	• Highest piezoelectric coefficients
2–2	• High acoustic impedance backing • Easy of efficient poling
1–3	• Highest electrochemical coupling factors
Fiber composites	• Lightweight • Robustness • Increased actuation strain energy density

4.1 Polymer Matrix

Detailed information of the more relevant piezoelectric polymers used as matrices in the development of polymer composites is provided in Table 3. These are classified into two categories: amorphous and semi-crystalline. Each polymer is associated with specific dielectric values and piezoelectric coefficients. When it comes to semi-crystalline polymers, their piezoelectric properties can be attributed to the crystalline phase, together with some contribution from the crystalline amorphous interface. This is where dipolar moments can align when subjected to an electric field [27].

PVDF, discovered in 1969, stands out as a semi-crystalline polymer with aligned chains forming dipoles within crystallites, surrounded by an amorphous matrix [28]. PVDF has proven effective in various applications due to its relatively high piezoelectric coefficient when crystallized in the electroactive β-phase, along with excellent electromechanical response, chemical stability, and low acoustic impedance [58, 59]. Its unique negative d_{33} (d_{33} ~ −30 pC/N) value sets it apart outperforming other polymers such as nylon-9, polyureas, poly-L-lactic acid (PLLA), and poly(b-hydroxybutyrate) (PHB) [60, 61]. PVDF is typically processed in the non-polar α-phase, when processed from the melt, the obtention of the polar β-phase typically requiring stretching, and later poling to enhance the macroscopic piezoelectric

Table 3 Main piezoelectric properties of different polymers [6, 27, 36]

Polymer	Piezoelectric coefficient d_{ij} $[pCN^{-1}]$	Piezoelectric voltage constant g_{33} $[VmN^{-1}]$	Electromechanical coupling coefficient k_{ij}
PVDF	$d_{33} = -24$ to -34 $d_{32} = 3$ $d_{31} = 8$ to 22	− 330	$k_{33} = 0.20$ $k_{31} = 0.12$
PVDF-TrFE	$d_{33} = -25$ to -40 $d_{31} = 12$ to 25	380	$k_{33} = 0.29$ $k_{31} = 0.16$
PVDF-HFP	$d_{33} = -24$ $d_{31} = 30$	–	$k_{33} = 0.36$ $k_{31} = 0.187$
PLLA	$d_{14} = 10$	g_{13} = 0.3–0.5 mV m/N	–
Polyamide	$d_{33} = 4$ $d_{31} = 14$ (100–200 °C)	–	$k_{31} = 0.049$
Cellulose	$d_{33} = 5.7$ $d_{31} = 1.88$ to 30.6 $d_{14} = -35$ to 60	–	–
Polyurethane	$d_{31} = 27.2$	–	–
Polyurea	$d_{33} = 10$ to 21 (25–180 °C) $d_{31} = 10$	–	$k_{31} = 0.09$
Polyimide	$d_{33} = 2.5 - 16.5$	–	–
PAN	$d_{31} = 2$	0.087	–
PVDC	$d_{31} = 0.5 - 1.3$	–	–

response [62]. The efficiency of this process depends on factors like the stretching ratio, temperature, filler type, and content, all of which contributing to the electroactive phase content and crystallinity of PVDF [63]. Innovative fabrication methods, such as ionic liquid-assisted fused deposition modeling, enable the printing of PVDF with a high β-phase content, eliminating the need for stretching and even poling [64]. Applications include a piezoelectric fabric for wearable energy harvesters and biomedical engineering scaffolds due to PVDF's flexibility and biocompatibility [65, 66]. Additionally, PVDF devices have been explored for macro-scale power generation from hydrokinetic energy in riverbeds, among others [67, 68].

Polyvinylidene fluoride-co-trifluoroethylene (PVDF-TrFE) stands out as a copolymer that spontaneously exhibits piezoelectricity without the need for stretching. Introducing defect groups into PVDF, the (PVDF-TrFE) copolymer facilitates direct crystallization of the electroactive β-phase during processing [69]. Despite having a lower dipole moment than PVDF, PVDF-TrFE's advantages in fabrication and piezoelectric applications make it superior [62, 70]. Applications include impact detectors, power harvesters, self-balancing robots, and flexible tactile sensors [70–72].

Polyamides, with nylon being the most used, exhibit significant piezoelectric response among ferroelectric polymers. Notably, nylon stands out among piezoelectric polymers as a well-established material in the industry, having been used in clothing since the 1940s. The revelation of polyamides' piezoelectric properties occurred in 1970 by Kawai et al. [36]. Further exploration by Scheinbeim and Newman, particularly in odd-numbered nylons, uncovered enhanced piezoelectric properties due to the unique arrangement of amide groups, whereas in even numbered polyamides dipole moments cancel out each other [73, 74]. Nylon opens thus the way for piezoelectric fabrics [75]. These fabrics can harness electric energy from movement, offering a sustainable power source for small electronic devices [76]. Nylon fabrics also find application in pressure sensing [77]. However, challenges include the need for the δ-phase for piezoelectricity, which is not achieved through conventional fabrication methods like melt extrusion, and their hydrophilic nature, with water adsorption affecting their piezoelectric properties [36].

Among bio-based polymers, one polymer that has awakened strong interest is poly-L-lactic acid (PLLA), after reports of piezoelectricity without the need of poling [50]. This is an optically active polymer proposed for biomedical applications due to its ability of being resolved and absorbed in a human body [78]. Piezoelectric response in PLLA is achieved when crystallites become oriented during fabrication process, most typically by cold drawing, associated with the polarity induced by carbonyl groups [79]. This avoids the need of a further poling treatment, unlike PVDF and polyamides, simplifying the manufacturing of polymer-based piezoelectric devices. Indeed, applications in sensing and energy harvesting have already been proposed based on PLLA. Nonetheless, its piezoelectric coefficients (d_{14} ~ 10 pC/N), as other alternative polymers considered so far, are lower than best PVDF-based copolymers.

Piezoelectricity has been also observed in amorphous polymers, in which the absence of crystalline phases means that polarization is achieved as molecular dipoles become locked in place. Some of the most commonly used amorphous polymers are polyimide, polyvinylidene chloride (PVDC), and poly (arylene ether nitrile) (PAEN) [27].

Polyimides are characterized by exceptional thermal, mechanical and dielectric properties [36]. While PVDF exhibits superior piezoelectric characteristics, polyimides surpass PVDF in applications involving higher temperatures, maintaining their piezoelectric performance up to 150 °C compared to PVDF's degradation beyond 70–80 °C [80]. As amorphous polymers with a high glass transition temperature, polyimides employ a distinct piezoelectric mechanism from semi-crystalline polymers [36]. The poling process involves subjecting the material to a high electric field at an elevated temperature to align the dipoles, followed by cooling below the glass temperature while maintaining the electric field. This process aims to retain a partially polarized state at lower temperatures, making polyimides suitable for microelectromechanical systems (MEMS) devices, high-temperature tactile sensors and pyroelectric sensors, where PVDF and fluoropolymers lack stability [81]. Polyimides also find application in piezoelectric nanogenerators (PENG) for electronic skins or biomedical devices [82].

4.2 Ceramic Fillers

High-performance piezoelectric ceramic materials, highlighted in Table 4, are known for their chemical inertness, high dielectric constants, but also their mechanical brittleness. Materials frequently used in polymer composites are PZT, BTO, zinc oxide (ZnO), and lead-free options like KNN. PZT features a complex phase diagram with a morphotropic phase boundary (MPB) at Zr/Ti = 52/48 separating two polymorphs of rhombohedral and tetragonal symmetries, in which lattice transverse softening was demonstrated, yielding very high polarizability and piezoelectric response [27]. Introduced in the early 1950s at the Tokyo Institute of Technology, PZT is a ferroelectric perovskite ceramic recognized for its exceptional electromechanical performance [83]. It is currently acknowledged that the large piezoelectric response is a direct consequence of the presence of a monoclinic Cm phase between the rhombohedral and tetragonal polymorphs, providing a structural bridge between them [84]. Further, it withstands elevated temperatures (Curie temperature about 350 °C), shows stability in various environments and application versatility from aerospace to microscopy [85, 86]. However, aside from the typical stiffness of ceramic materials, it contains lead, a major limitation for applicability [85]. Ongoing research explores PZT micro-sensors for energy harvesting, mindful of these constraints [86].

A main line of research at the cutting edge of the field is the development of lead-free alternatives, in order to comply with enforced environmental regulations that require the elimination of lead from electronic equipment. Efforts are concentrated also on perovskite solid solutions in which physical properties are considerably enhanced at the MPB, where two (or more) ferroelectric polymorphs might coexist [35]. Three families of perovskites, among the most topical lead-free ones under

Table 4 Main piezoelectric properties of different piezoelectric ceramics [27, 36]

Ceramic	Piezoelectric coefficient d_{ij} $[pCN^{-1}]$	Piezoelectric voltage constant g_{33} $[VmN^{-1}]$	Electromagnetic coupling coefficient k_{ij}
PZT	$d_{33} = 100 - 1000$	0.025	0.6–0.7
KNN	$d_{33} = 80 - 160$	0.0469	0.51
$BaTiO_3$	$d_{33} = 191$ $d_{31} = -78$	0.01114	0.49
ZnO	$d_{33} = 5.9$ $d_{31} = -5$	–	–
BNT	$d_{33} = 75$	–	0.21
AIN	$d_{33} = 5$	0.1	0.23
BCZT	$d_{33} > 500$	–	–

consideration for piezoelectric applications, are: alkali niobates, barium titanates and bismuth-containing compositions.

Perhaps the most promising lead-free ferroelectric material and doubtless biocompatible is KNN, in which huge attention has been paid over the last decade after reports on high piezoelectric coefficients [87], especially in some Li,Ta-modified compositions prepared by innovative techniques like reactive template grain growth (RTGG), where properties achieved were comparable to those of PZT [46]. Recent studies demonstrated remarkable piezoelectric constants up to 700 pC N^{-1} with a high Curie temperature of 242 °C [88]. Its main drawbacks are the need for careful handling of highly-hygroscopic powders, and difficult control of stoichiometry due to volatility of alkali species with a direct effect on properties. Notably, KNN's composition makes it safe for applications such as medical implants and energy harvesting, emphasizing its environmental advantage [86].

$BaTiO_3$, the first perovskite-structured ferroelectric material discovered during World War II, gained early recognition due to its high dielectric constant [89]. Initially not known for its piezoelectric properties, strong improvements have been achieved based on reducing domain size and A/B-site substitutions [90]. For instance, hydrothermally grown BTO with a 1–2 μm grain size achieved a notable d_{33} value of 460 pC N^{-1}. Alternatively, Ca, Zr co-doped BTO has emerged as leading lead-free candidate owing to reported high piezoelectric coefficients, above 600 pC N^{-1}, that match those of commercially available high-sensitivity soft PZT [90, 91], though the operation temperature range is rather short due to its low Curie temperature, which could be a limitation for many applications. Most applications where the usage of BTO ceramics may be envisaged, like energy harvesting or biomedical field [92], demand a robust material reliability.

Bi-containing perovskites are also playing a major role in current research strategies. The presence of highly polarizable bismuth cations with unshared electronic pair at A-site is considered essential for obtaining large polarizability and high piezoelectric response [93]. This has concentrated further attention towards $Bi_{1/2}Na_{1/2}TiO_3$-based materials, for which large electromechanical response and piezo-strain coefficients above 500 pC N^{-1} have been reported, though related to phase-change phenomena rather than to the piezoelectric effect. $BiFeO_3$-based systems have also showed enhancement d_{33} owing to field-induced ordering of nanoscale domain structures. It is important to highlight that Bi-containing perovskites have demonstrated very good down-scaling behavior of properties among lead-free systems, which plays a fundamental role in piezoelectric ceramic technologies that are no oblivious to miniaturization in microelectronics [49].

Composites with ZnO fillers offer enhanced dielectric and piezoelectric properties along with photocatalytic behavior. Nanostructured piezoelectric materials offer improved energy conversion efficiency compared to macroscale counterparts, particularly in low-frequency vibrations. This is attributed to their ability to withstand higher strain, resulting in increased voltage output. ZnO nanostructures, ranging from 20 to 100 nm in diameter, exhibit excellent piezoelectric properties and find applications in self-powered devices [94]. Aligned ZnO nanowires, grown through the vapor–liquid-solid process, demonstrate a higher effective piezoelectric constant than bulk, with nanowire diameter influencing the piezoelectric constant [36]. These nanostructures have been utilized to power nanotube-based devices and rapidly respond to external forces. As representative example, ZnO nanorods on conducting textiles generate a 1.81 V output at 26 Hz, sufficient to activate an LCD display [95].

Other ceramic fillers also used in polymer composites are aluminum nitride (AIN) or lithium niobate ($LiNbO_3$), among others [36]. The combination of ceramic fillers with piezoelectric polymers results in composites with improved thermal and electrical properties while retaining excellent mechanical characteristics. The size of ceramic particles allows the production of micro or nanocomposites tailored for specific applications. Processing conditions influence morphology and properties, with printing technologies enabling cost-effective production of large-area composite materials [27].

Magnetoelectric composites, formed by blending piezoelectric polymers, such as PVDF and copolymers, with magnetic fillers like $Zn_{0.2}Mn_{0.8}Fe_2O_4$ (ZMFO) or $CoFe_2O_4$ (CFO), seamlessly integrate piezoelectric and magnetostrictive features [56]. Also, the search of environmentally-friendly alternatives free of toxic elements like Ni and Co is playing an important role, ideally biocompatible. This dynamic synergy enables the manipulation of electrical polarization through magnetic fields and vice versa, resulting in a powerful magnetoelectric response. Ongoing research explores diverse applications for these composites, ranging from sensors, data memories, and energy collectors to biomedical devices, promising innovative solutions across various domains [27].