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FEATURE ARTICLE

Polymer-Based Magnetoelectric Materials

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Polymer-based magnetoelectric (ME) materials are an interesting, challenging and innovative research field, that will bridge the gap between fundamental research and applications in the near future. Here, the current state of the art on the different materials, the used configurations for the development of sensors and actuators, as well as the main values of the ME coupling obtained for the different polymer-based systems are summarized. Further, some of the specific applications that are being developed for those polymer-based ME materials are addressed as well as the main advantages and remaining challenges in this research field.

1. Introduction

The magnetoelectric (ME) effect, defined as the variation of the electrical polarization of a material in the presence of an applied magnetic field or as the induced magnetization in the presence of an applied electric field,[1–3] can be seen as the bridge between the electric and magnetic properties of matter.[4] The ME effect has drawn increasing interest due to its potential applications in areas such as information storage, spintronics, multiple-state memories, sensors, actuators, transformers, gyrators, microwave devices, optical waves, diodes, among others.[4–8]

In order to positively match the technological requirements of these and other applications, a strong ME effect at room temperature has been obtained from multiferroic (MF) composites, which is generally obtained by combining piezoelectric and magnetostrictive components.[9]

Different from what happens with the single-phase ME materials so far available at room temperature, the larger design flexibility of MF composites allows the introduction of multifunctional properties in which the coupling interaction between the piezoelectric and magnetostrictive components produces an ME response several orders of magnitude higher than those in single-phase ME materials.[10]

The ME effect in such composites is a product tensor property which results from the cross interaction between the piezoelectric and magnetostrictive phases in the multiferroic ME composite, whereas the sum and scaling properties denote the average or the enhancement of effects which are already present in the constituent phases.[5] In this way, composites can be used to generate an ME response from the combination of materials which themselves do not allow the ME phenomenon.[4]

Once a magnetic field is applied to the composite, strain in the magnetostrictive phase is induced. This is transmitted to the piezoelectric constituent, which undegoes a change in electrical polarization. In an analogous way, the reverse effect can occur: when an electric field is applied to the composite, strain is induced in the piezoelectric phase which is transmitted to the magnetostrictive phase, leading to a change in the magnetization. The above mentioned coupling mechanism can be written as:[11]

$$\mathrm{ME_H} = \frac{\text{magnetic}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{electric}} \tag{1a}$$

or,

$$\mathrm{ME_E} = \frac{\text{electric}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{magnetic}} \tag{1b}$$

Equation 1 shows the coupling of the electric and magnetic orders trough an elastic interaction. Therefore, the ME response in MF composites is an extrinsic effect, dependent on the composite's microstructure and the coupling interaction across the magnetostrictive and piezoelectric interfaces.[12]

Based on this property and the large ME effect obtained at room temperature for some composites, some prototype ME devices have been proposed.[13]

Since the field of research described in this Feature Article has a complex taxonomy and typically involves terms from different fields,[3] the basic concepts of the ME research field are listed and defined in **Table 1**.

This Feature Article will provide an overview on the historical developments and a discussion on the main achievements in the ME research field during the last decades, and will then mainly focus on polymer-based ME materials. Three main types of polymer-based ME materials, nanocomposites (**Figure 1**a), laminated composites (Figure 1b), and polymer as a binder composites (Figure 1c) will be then discussed.

Then, the obtained ME coefficients for polymer-based ME materials will be ordered by composite type and some of the main possible applications will be discussed. Finally, this Feature Article will end with some concluding remarks and a summary of the distribution of the maximum polymer-based ME coefficient by reference, type, and DC magnetic field.

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1.1. History

Four years (1888, 1894, 1905, and 1926) were pivotal in the emergence of the ME research field (**Figure 2**):

In 1888, Röntgen, before winning the Nobel Prize due to the discovery of the X-rays, observed that a dielectric moving in a electric field became magnetized.[32] The reverse effect, the electrical polarization of a dielectric moving in a magnetic field was discovered by Wilson in 1905.[33] Between the first and second discoveries indicted above, Pierre Curie, in 1894, based on symmetry considerations enunciated the possibility of ME effect in non-moving crystals.[4,34] In 1926, Debye introduced and coined the term "magnetoelectricity" for the effect that was not successfully proved experimentally at that time.[35] n 1959, the ME effect was predicted to occur in chromium oxide (Cr_2O_3) by Dzyaloshinskii,[36] prediction that was experimentally confirmed in the following year by Astrov.[37] In 1966, the group of Ascher and Schmidt at the Battelle Institute in Geneva and Newnham at the Pennsylvania State University discovered a high number of ME boracites[38] and phosphates.[39]

ME coupling coefficients, defined as

$$\alpha = \frac{\partial P}{\partial H} \tag{2}$$

were not as high as necessary for applications, but the number of new ME materials increased significantly.

In 1973, scientific work on ME materials reached a saturation point since it was felt that single-phase MEs were not technologically applicable due to the weak ME coupling and the need of very low temperatures. Furthermore, the theoretical considerations gave no indication or hope of significant improvements.[40] As a result of this dead-end, the intensity of ME scientific activity strongly declined for almost 20 years.

In the 1990s, interest in ME materials strongly increased again due to the relationship between the ME and MF composites: the main object of scientific investigations into the ME shifted from single phase ME materials, to the search for MF compounds with higher ME coupling.[41] In those novel composites, the ME response is due to elastic coupling between the two constituent phases, one piezoelectric and the other magnetostrictive.[5]

Three main types of bulk magnetoelectric composites have been investigated both experimentally and theoretically: a) magnetic metals/alloys e.g., laminated Terfenol-D or Metglas and piezoelectric ceramics such as lead zirconate titanate; b) laminated Terfenol-D and Metglas and piezoelectric polymers; and c) particulate composites of ferrite and piezoelectric ceramics.[42]

Today, ME research is a strong research area, showing still plenty of mysteries, promises, and challenges. One of them is to replace the ceramic in bimorphs or superlattice composites by a polymer or polymer-based piezoelectric matrix to achieve larger areas or non-planar structures.[13]

1.2. Non Polymeric ME Materials: Problems Regarding Application Developments

The magnitude of the ME coupling coefficient in most of the single phase MF materials is in the range of 1–20 mV/(cm Oe) which is considered insufficient for most of the proposed practical applications.[43] In addition, there is a wide variation of the transition temperatures (paraelectric to ferroelectric, paramagnetic to antiferromagnetic, antiferromagnetic to ferromagnetic) for the single-phase ME materials and a limited number of materials that exhibits ME behavior at room temperature.[44] In this way, most of these MEs can be only used at low temperatures (≈10 K), which severely hinders the design and applications of devices.

Despite ME coefficients obtained in ceramic MF composites being three orders of magnitude higher than in single phase materials,[45] such composites may become fragile and are limited by deleterious reactions at the interface regions, leading to low electrical resistivity and high dielectric losses >0.1, hindering in this way the incorporation into devices.[11] Apart from the aforementioned disadvantages, ceramic composites still have other problems such as being expensive, dense and brittle, which can lead to failure during operation.[46,47] In this way, ceramic-based ME materials are not attractive from a technological point of view.

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Table 1. ME basic concepts.

Concept	Definition	References
Mutiferroic	Material that possesses two or all three ferroic properties (ferroelectricity, ferromagnetism and ferroelasticity).	[14,15]
Ferroelectric	Material that possesses a spontaneous and stable polarization that can be hysteretically switched by an applied electric field.	[16,17]
Ferromagnetic	Material that possesses a spontaneous and stable magnetization that can be hysteretically switched by an applied magnetic field.	[18,19]
Ferroelastic	Material that possesses a spontaneous and stable deformation that can be hysteretically switched by an applied stress.	[20,21]
Piezoelectricity	Variation of the strain of a material as a linear function of an applied electric field or a change in the material polarization as a linear function of applied stress.	[21,22]
Piezomagnetism	Variation of the strain of a material as a linear function of an applied magnetic field or a change in the material magnetization as a linear function of applied stress.	[23,24]
Electrostriction	Variation of the strain of a material as a quadratic function of an applied electric field.	[25,26]
Magnetostriction	Variation of the strain of a material as a quadratic function of an applied magnetic field.	[27,28]
Piezoelectric coefficient	Relates the mechanical strains produced by an applied electric field and is called the strain constant, or the "d" coefficient. d is a tensor, with components d_{ij}, where i indicates the direction of polarization generated in the material when the electric field is zero (or the direction of the applied field), and j is the direction of the applied stress (or the induced strain).	[25,26]
Piezomagnetic coefficient	Relates the mechanical strains produced by an applied magnetic field and is called the "d_m" coefficient. d is a tensor, with components d_{ij}, where i indicates the direction of magnetization generated in the material when the magnetic field is zero (or the direction of the applied field), and j is the direction of the applied stress (or the induced strain).	[27,29]
Magnetostrictive coefficient	Relates the mechanical strains produced by an applied magnetic field and is called the "λ" coefficient. λ is a tensor, with components λ_{ij}, where i indicates the direction of magnetization generated in the material when the magnetic field is zero (or the direction of the magnetic field), and j is the direction of the applied stress (or the induced strain).	[27,28]
Magnetoelectric coefficient	Relates the polarization/voltage produced by an applied magnetic field and is called the "α" coefficient. α is a tensor, with components α_{ij}, where i indicates the direction of polarization/voltage generated in the material when the electric field is zero (or the direction of the applied electric field), and j is the direction of the applied magnetic field (or the induced magnetization).	[30,31]

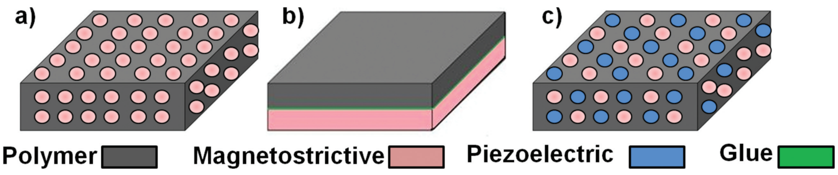

Figure 1. Types of polymer-based ME materials: a) nanocomposites, b) laminated composites, and c) polymer as a binder composites.

A more recent approach to obtain highly flexible and nonbrittle ME composites and to solve all the aforementioned problems is to use polymer-based nanocomposites.[13,48] In comparison with the ceramic ME composites, polymer-based ME materials can be easily fabricated by conventional low-temperature processing into a variety of forms, such as thin sheets or molded shapes, and can exhibit improved mechanical properties.[13]

2. Polymer-Based Magnetoelectric Materials

As previously mentioned, three main types of magnetoelectric polymer-based composites can be found in the literature: nanocomposites, polymer as a binder, and laminated composites. In the following section, the main characteristics, materials, achievements, and limitations of each type will be discussed.

2.1. Preparation of Polymer-Based ME Materials and Interface Effects

Regarding the preparation of particulate polymer-based ME nanocomposites, two distinct polymers have been used, polyurethane (PU) and poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)), a copolymer of PVDF.

MF PU films are usually obtained by the solution cast method. In such method, PU granules are first dissolved in a solvent (typically N,N-dimethylformamide (DMF)) at 75 °C for 1 h. Then, the desired amount of magnetic fillers is added to the polymer solution and a mechanical stirring process is performed. Finally, the obtained solution is poured onto a clean glass substrate and degassed to eliminate voids and dried at 70 °C.[49]

Concerning the fabrication of P(VDF-TrFE based MF films, two different methods have been reported in refs [42,50,51]. In the method presented by Martins et al.,[42,50] the desired amount of magnetostrictive nanoparticles is added to DMF and the obtained mixture is then placed in an ultrasound bath to ensure that nanoparticles are well dispersed in the solution and also to avoid loose aggregates.[23] Afterwards, P(VDF-TrFE) powder is added. Further, the obtained mixture is placed in a Teflon mechanical stirrer with ultrasound bath for complete dissolution of the polymer. Flexible films are obtained by spreading the solution on a clean glass substrate. Solvent evaporation and polymer crystallization are performed inside an oven at controlled

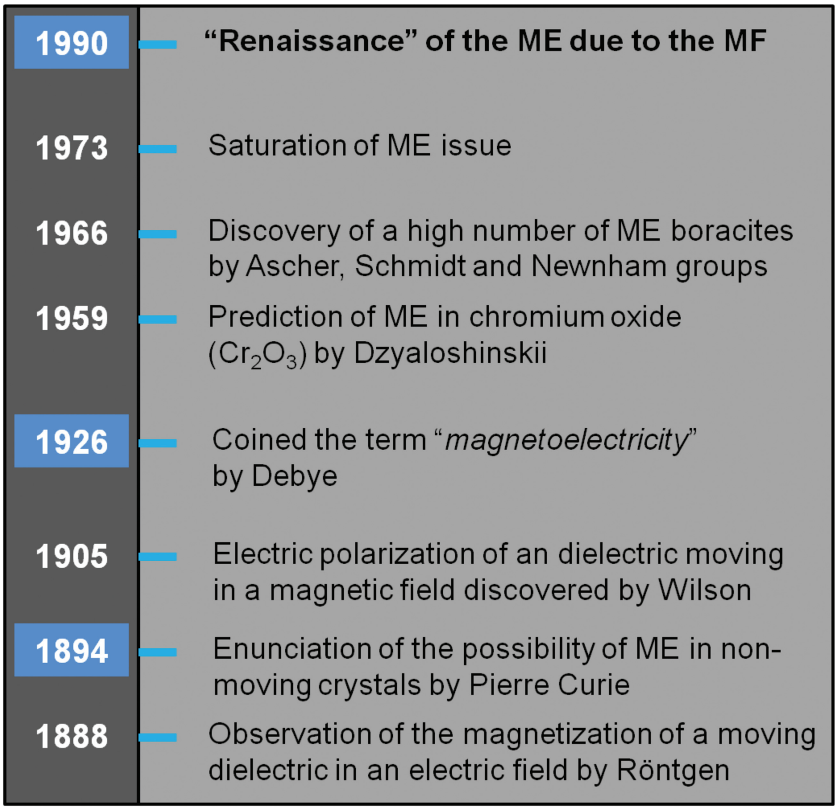

Figure 2. Highlights in the investigation of the ME effect.

temperature and crystallization is achieved by cooling down the samples to room temperature.

Alternatively, as reported in ref [51], magnetostrictive nanoparticles are dispersed in the P(VDF-TrFE) solution matrix in an ultrasound bath. The P(VDF-TrFE) solution is previously prepared by dissolving P(VDF-TrFE) pallets into methyl-ethyl-ketone (MEK). After vacuum and thermal treatments, the final crystallized MF films are obtained. Since electrical polarization is essential to obtain piezoelectric responses, the MF films are electrically poled by submitting the films to high electric fields (900 kV/cm as a maximum strength).

The synthesis of the magnetostrictive nanoparticles used in polymer-based ME particulate nanocomposites is well discussed in the literature.[52–57] On the other hand, the interface effects between nanoparticles and the polymer matrix has received only little attention. In this kind of MF nanocomposite, the characteristics of the interface becomes a prominent factor[58] in determining the magnetoelectroelastic properties as well as the ME effect of the MF nanocomposite, due to the increasing ratio of the interfacial area to volume.

In recent years, surface elasticity theory[59] has been developed to account for the effects of surfaces and interfaces at the nanometer-scale. These studies show that depending upon the interface design, the effective properties of the nanocomposites can be either enhanced or reduced.[60] In this way, taking advantage of the theory of linear elasticity, it was found that the interfacial stress displays short-range effect on the stress state in nanocomposites, which introduces internal stresses in both the matrix and the inclusion and leads to changes in the displacement field and the stress field created by a external loading. Shrinkage of the inclusion was also observed. Unlike the classical results, in the theory of linear elasticity, the effective bulk modulus is a function of the interfacial stress and the size of the inclusion.[61]

The nonclassical interface condition has also been studied by Pan et al.[60] and it was observed that such interface condition exerts a significant influence on the local and overall magnetoelectroelastic responses of MF composites, in particular when the fillers are at the nanometer-scale. It was also demonstrated that it was possible to enhance the ME coefficient of a MF composite consisting of magnetostrictive fillers reinforced in a piezoelectric matrix by designing an electrically highly conducting interface.

Keeping the interface of nanocomposites as subject of study, but in an more experimental approach, Nan et al.[62] have investigated the role of the Terfenol-D/polymer interface layer, induced by surfactant modification of the Terfenol-D particle surfaces, in the ME properties of the composites. It was reported that by adding a silane surfactant to the surface of the nanoparticles, the piezoelectricity of the composite is diminished since the surfactant modification leads to a reduction of the piezoelectric response. Thus, such an inactive interface is even more harmful to the ME response of the composites. A proper Terfenol-D particles/polymer interface ensures the perfect coupling between these phases, transferring elastic strains without appreciable losses. Any imperfect interfaces will roughly decrease the displacement transfer capability, thereby leading to a decrease in the ME response of the composites.

Continuing their study on the effects of the interface on the ME response of Terfenol-D/P(VDF-TrFE) layered composites, Nan et al.[63] discussed the effective coupling properties of such composite. This coupling was expressed in a convenient matrix formulation by using the Green's function technique. Imperfect interfaces between Terfenol-D and P(VDF-TrFE) phases would decrease the displacement transfer capability, thereby leading to a decrease in the ME response of the composites. In particular, when the particle sizes were at the nanometer scale, the effect of the imperfect interface would be more pronounced due to a large amount of interfaces in the composites. However, in the technologically important piezoelectric ceramic/epoxy and magnetostrictive composites that have been extensively investigated, the quantitative correlation between the coupling behavior for composites and their interface imperfection remains to be explored.

Theoretical calculations of the ME properties in a three-phase MF particulate composite of Terfenol-D, lead-zirconate-titanate (PZT), and polymer has been also reported[64] based on the Green's function technique. It was shown that the values of the ME voltage coefficients are very sensitive to mechanical boundary conditions of the composite sample, and that the polarization orientation in PZT particles and the inactive interfacial layer surrounding PZT particles have a significant effect on the ME response of the composite. The quantitative analysis of the effect of such mechanical boundary conditions in the ME response of the composites will be later discussed in this article. Interface effects have been already addressed in inorganic ME composites. In particular, additional to the interface effects in the ME response of $BaTiO_3/NiFe_{1.98}O_4$ nanocomposites, Sreenivasulu et al.[65] also reported the size effects. It was observed that the particulate $BaTiO_3/NiFe_{1.98}O_4$ nanocomposites exhibit large ME coefficient values (about five times larger) than the $BaTiO_3/NiFe_{1.98}O_4$ microcomposites due to the large piezoelastic dynamic strain coefficients and an adequate interface contact between both $BaTiO_3$ and $NiFe_{1.98}O_4$ phases. The magnetostriction was higher in nanograined $NiFe_{1.98}O_4$ than micrograined $NiFe_{1.98}O_4$ and thus, the magnetostrictive dynamic coefficient was proposed to have large values for nanocomposites than the microcomposites of similar compositions.

Regarding the experimental study of the interface and size effects on the ME properties of polymer-based ME nanocomposites and polymer as a binder composites it is therefore observed a clear need of further investigation. A systematic and exhaustive study of the effect of the PVDF/ferrite interface has been nevertheless reported concerning the nucleation of the electroactive β-phase of PVDF, and consequently in their ferroelectric, piezoelectric and ME properties.[66–70]

An interesting outcome of this investigation on PVDF/ferrite composites is the fact that the ferrite nanoparticles used as the magnetostrictive phase in the ME nanocomposites have the ability to nucleate the electroactive β-phase of PVDF,[66] due to the electrical interactions between the negative nanoparticle surfaces and the positively charged polymeric CH_2 groups[69,71]. This fact will allow to reduce the production costs of the polymer-based ME nanocomposites,[72] leading to the development of applications of such as didactics, toys and disposable devices.[13] Focusing on layered or laminate ME structures, those configurations are usually obtained by gluing together the electroactive polymer and the magnetostrictive phase using an epoxy binder[9,73–76] by the direct deposition of one phase on top of the other,[77,78] or by hot-molding techniques.[79,80]

In such ME layered composites, the quality of the interface that is determined by the interface coupling parameter is only dependent on surface inhomogeneities and interactions between constituents during the preparation as well as misfit strains. Such a parameter is a measure of differential deformation between the piezoelectric and magnetostrictive layers and $k = 1$ for an ideal interface and $k = 0$ for the case without coupling.[5]

Based on modified constitutive equations and the finite element method, the quality of the MF interface has been studied.[81] It was verified that the ME effect of laminated magnetostrictive/piezoelectric MF nanocomposites was remarkably dependent on the thickness and characteristics of binder layer. Based on the constitutive equations, results show that, when the interfacial layer is somewhat stiff and the binder layer is thin, a large ME effect will be produced.

In order to treat such an interfacial bonding effect, Nan et al.[82] changed the shear modulus and the relative thickness of the conductive epoxy used for bonding the piezoelectric and magnetostrictive components of a MF layered composite. The increase in the thickness of the conductive epoxy films between the piezoelectric and magnetostrictive phase leads to a decrease in the ME voltage coefficients, since the conductive epoxy films are ME inert. It was also reported that a very low ratio between the thickness of epoxy and thickness of the MF composite (<0.001) is good enough for producing a giant ME response. It was also discovered that the elastic modulus of the ME inert epoxy films has a significant effect on the ME response values, by decreasing the shear modulus of the thin epoxy films, i.e., using a very flexible epoxy as the binder, the interfacial bonding between the piezoeletric and magnetostrictive components becomes weak due to the formation of a sliding interface. The weak interfacial contact would lead to appreciable losses of transferring elastic strain/stress from the piezoelectric component to the magnetostrictive component, and thus the decrease in the shear modulus of the thin interfacial epoxy films results in a large decrease in the ME response of the composites. As expected, any imperfect interfacial bonding produced by the epoxy binders would decrease the displacement transfer capability, thereby leading to a decrease in the ME response of the layered composites.

Another type of interface ME coupling has been implemented by Rondinelli et al.[83] It was demonstrated that the ME effect can arise from a carrier-mediated mechanism. In such case, the magnetic response is mediated by the accumulation of spin-polarized carriers at the interface between a nonmagnetic dielectric and a ferromagnetic metal. For the ferromagnetic/dielectric interface, this kind of ME effect is linear with respect to applied electric field and the magnitude is two orders lower than that for the interface bonding mechanism.

In the case of ferromagnetic/ferroelectric heterointerfaces, most of the studies have been reported in all the inorganic ME composites, though it is expected that the main behaviors are similar for polymer-based ME materials. For example, in the inorganic ME composite $SrRuO_3/BaTiO_3$ interface,[84] the ME effect can be further enhanced owing to field effect and nonlinear variation of the ferroelectric polarization with applied electric field. Experimental manifestation of the predicted ME effects driven by these purely electronic mechanisms were later reported for the $La_{0.8}Sr_{0.2}MnO_3/PbZr_{0.2}Ti_{0.8}O_3$ bilayers.[85] More recently, the interface bonding ME effect was verified by the observation of room-temperature multiferroicity at the interfaces of $BaTiO_3$ ultrathin film with Fe or Co.[86,87]

Contrary to the case of $Fe/BaTiO_3$ system mentioned above, the $Ni/BaTiO_3$ structure reported by Dai et al.,[87] has shown a novel type of interface bonding ME effect, which is determined by the change of magnetic moments on Ni atoms near the interface, and that there existed an extraordinary intralayer oscillation of magnetic moments within the Ni layer. Furthermore, it was demonstrated that the underlying physics was due to the different interfacial electronic structure and the different type of magnetic interaction.[87]

Changing the Ni component reported by Dai et al. to the Fe, density-functional calculations were employed by Lukashev et al.,[88] to investigate the effect of ferroelectric polarization of $BaTiO_3$ on the magnetocrystalline anisotropy of the $Fe/BaTiO_3$ interface. It was found that the interface magnetocrystalline anisotropy energy decreased (from 1.33 to 1.02 erg cm^{-2}) when the ferroelectric polarization was reversed. This strong ME coupling was explained in terms of the changing population of the Fe 3d orbitals at the Fe/BaTiO3 interface driven by polarization reversal.

It has been also reported,[89] that organic ferroelectrics, such as PVDF, have an additional advantage of being weakly bonded to the ferromagnet, thus minimizing undesirable effects such as interface chemical modification and/or strain coupling. By using first-principles density functional calculations of Co/PVDF heterostructures it was demonstrated the effect of ferroelectric polarization of PVDF on the interface magnetocrystalline anisotropy that controls the magnetization orientation. It was shown that switching of the polarization direction alters the magnetocrystalline anisotropy energy of the adjacent Co layer by ≈50%, driven by the modification of the screening charge induced by ferroelectric polarization. The effect was reduced with Co oxidation at the interface due to quenching the interface magnetization.

In this way, ref. [89] indicates that the electronically assisted ME effects at the ferromagnetic/ferroelectric interfaces may be a viable alternative to the strain mediated coupling in related heterostructures and the electric field-induced effects on the interface magnetic anisotropy in ferromagnet/dielectric structures.

The influence of interfacial effects on the ME properties of PVDF based ME composites was also studied in the reference.[77] Flexible Sm–Fe/PVDF laminate composites were prepared by depositing of Sm–Fe nanoclusters onto the PVDF film using cluster beam deposition method. Since there was a small amount of residual argon carrier gas molecules in the Sm–Fe/PVDF film, it was actually subjected to a residual compressive stress. Accordingly, under the combination influence of negative magnetostriction and compressive stress, the Sm–Fe film could also generate the magnetic anisotropy with an in-plane magnetic easy axis, which allows a more efficient magnetic-mechanical-electric coupling along the interface.

2.2. Particulate Nanocomposites

When compared to their ceramic ME counterparts, a much smaller variety of 0–3 type ME polymer-based nanocomposites have been reported in the last two decades. Polymers such as piezoelectric PVDF and PU have been used in such ME nanocomposites due to their good piezoelectric/electrostrictive properties.[90,91]

In the electrostrictive PU-based ME composites several interesting results have been obtained, including the extraction of the true ME current from the total output current response and the coexistence of both linear and quadratic ME responses in the filled PU film. The obtained linear ME effect is of the same order of magnitude as that of the Cr_2O_3 single crystal (up to 18 mV cm^{-1} Oe^{-1}) and a possible linear magnetoelastoelectric coupling between fillers and polymer matrix not triggered by magnetostriction has been also proposed.[92]

The linear voltage ME coefficients obtained in PU/Fe_3O_4 and PU/Nickel composites were 11.4 and 6.0 mV cm^{-1} Oe^{-1}, respectively at 7 Hz, 0 DC field and 1 Oe AC field. Even when it is predicted that due to the magnetostriction it should be found an optimal value of H_{DC} and therefore a peak in the α value vs H_{DC} plot,[42,93] experiments show that α remains more or less constant with increasing H_{DC}. This experimental observation strongly suggested that the magnetostrictive properties of the material have no influence in the PU/Fe_3O_4 and PU/Nickel ME composites. This interesting fact has been confirmed as the ME response in PU composites is independent of the magnetostrictive properties of the fillers such as Terfenol-D, Fe_3O_4 or Nickel.[49] In this way, the ME coupling does not have its origin in the magnetostriction of the particles but rather in the linear elastic interaction between those particle aggregates and the highly polar microdomains of the semi-crystalline polymer PU.[93–95] Consequently, the coupling in PU composites is mainly due to the particular nature of the elastomer PU matrix composed of both rubbery and polar domains. A support for the aforementioned mechanism is the fact that the simple addition of morphous carbon nanopowder into PU based ME composites enhances the quasistatic strain amplitude[96] since the bonding between the PU polymer and carbon nanopowder prevents slippage and effectively improves the strain in the nanocomposite.[97] In any case, the origin of the ME coupling in such nanocomposites is not yet clearly established.[6]

Regarding the use PVDF as the piezoelectric constituent of ME nanocomposites and after the theoretical calculations of giant ME on ferromagnetic rare-earth-iron-alloys-filled ferroelectric polymers in 2001 by Nan et al.,[63,98] two main experimental reports can be found in the literature. Martins et al. introduced $CoFe_2O_4$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles into a polymer matrix of (P(VDF-TrFE). P(VDF-TrFE) was used instead of PVDF since the copolymers of PVDF, containing VDF molar percentages between 55 and 82, crystallizes from the melt in the ferroelectric phase which is an essential factor for the preparation of PVDF based ME nanocomposites.[99–100] The P(VDF-TrFE)/ferrite nanocomposites exhibit ferroelectric, piezoelectric, magnetic and direct ME effect dependent on the ferrite loading. In the case of P(VDF-TrFE)/$CoFe_2O_4$ nanocomposite, the resultant MF films showed saturated hard magnetic properties, improved polarization and piezoelectric response and a maximum α_{33} value of 41.3 mV cm^{-1} Oe^{-1}. On the other hand, for P(VDF-TrFE)/$Ni_{0.5}Zn_{0.5}Fe_2O_4$ composites, α_{33} increases linearly with applied H_{DC} and a 1.35 mV cm^{-1} Oe^{-1} maximum value was obtained for samples with 15 wt% ferrite.[50]

In contrast to PU based composites,[49] the ME P(VDF-TrFE)/$CoFe_2O_4$ response is strongly influenced by the magnetostriction of the ferrite nanoparticles since an optimal value of the H_{DC} magnetic field was observed and consequently a peak on the α value vs H_{DC} plot appears (**Figure 3**). The observed difference between the in plane and out-of-plane ME response of P(VDF-TrFE)/$CoFe_2O_4$ nanocomposites was fully attributed to the difference in the d_{33} and d_{31} P(VDF-TrFE) piezoelectric constants.[101]

Zhang et al. studied the effect of $CoFe_2O_4$ nanoparticles on the morphology, ferroelectric, magnetic and ME behaviors of P(VDF-TrFE)/$CoFe_2O_4$ nanocomposites. Once again, the ferroelectric and ME responses are strongly influenced by the concentration of ferrite nanoparticles.[51] A significant experimental α_{33} value around 40 mV cm^{-1} Oe^{-1} was obtained in this kind of nanocomposites. Both experimental ME voltage coefficients of Martins et al. and Zhang et al. were theoretical confirmed by a relatively simple model based on those of Wong

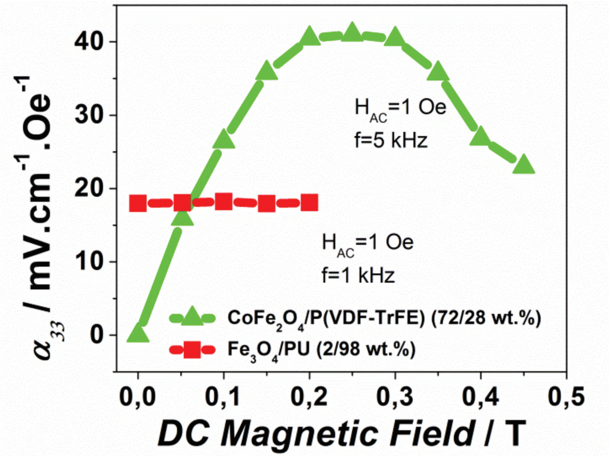

Figure 3. Comparison between the responses of P(VDF-TrFE)/$CoFe_2O_4$ (data from ref. [42]) and PU/Fe_3O_4 ME nanocomposites (data from ref. [49]).

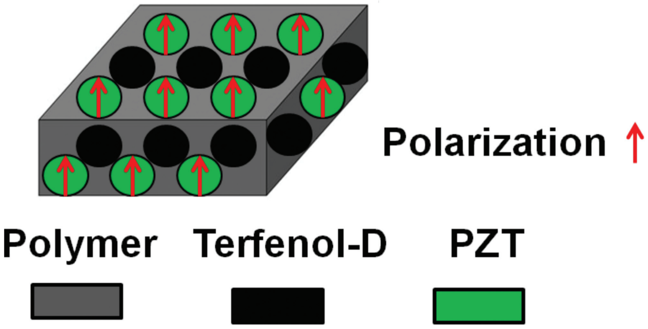

Figure 4. Schematic representation of the particulate Terfenol-D/PZT/polymer composites (based on an experimental description reported in ref. [64]).

and Shin[102] and Zhou and Shin.[103] In this model, the ME response α_{33} can be expressed as:

$$\alpha_{33} = (1-\phi)\frac{L_E}{\varepsilon}\left(d_{31p}\frac{dY_{xp}}{dH_m} + d_{32p}\frac{dT_{yp}}{dH_m} + d_{33p}\frac{dT_{zp}}{dH_M}\right)\left(\frac{dH_m}{dH}\right) \tag{3}$$

where L_E and $\frac{dH_p}{dH}$ are given by:

$$L_E = \frac{[\varepsilon_m + 2\varepsilon_p]]}{[(1-\phi)\,\varepsilon_m + (2+\phi)\,\varepsilon_p]} \tag{4}$$

$$\frac{dH_p}{dH} = \frac{3\xi_p}{(1-\phi)\left(\xi_m + \frac{dM_m}{dH_m}\right) + (2+\phi)\,\xi_p} \tag{5}$$

Here, p and m indicate the polymer and magnetic phase respectively; d_{3n} the piezoelectric coefficients; ε the dielectric constant, ϕ the volume fraction of the magnetostrictive phase; T and H are the stress and applied magnetic field, respectively; ξ the magnetic permeability and M the magnetization. $\frac{dM_m}{dH_m}$ is obtained from the magnetization curve of the nanocomposites.

Possible ME polymer-based nanocomposite structures were also synthesized using conducting polyaniline and nanosized $BiFeO_3$ particles through in situ sol–gel polymerization by Hemalatha et al.[104] The morphology, crystalline structure, magnetic, and optical properties of polyaniline/$BiFeO_3$ composites with various concentrations of nanofiller were discussed but the ME response of such nanocomposites has not yet been reported.

2.3. Polymer as a Binder Composites

Unlike in the previous section, in the polymer as a binder composites the polymer is not used as the piezoelectric phase of the ME material but as a binder for the piezoelectric and magnetostrictive particles that keep them together and provides the stress coupling between the piezoelectric matrix and the magnetostrictive fillers.

Three-phase particulate composites of Tefenol-D alloy, PZT and PVDF[72] (**Figure 4**) were the first to be studied.

In order obtain the ME response, a small volume fraction, f, of Terfenol-D nanoparticles were dispersed in a PZT/PVDF mixture by a simple blending technique and the obtained dielectric, piezoelectric and ME properties demonstrate that a percolation transition occurs at $f \approx 0.12$. When f is lower than 0.07 the MF composites exhibit good piezoelectric and ME responses but when $0.07 \leq f \leq 0.12$ the piezoelectric and ME response sharply drops and disappears at the percolation threshold, above which the composite becomes a conductor and only respond magnetostrictively. The maximum obtained value for α_{33} at 2KOe was about 42 mV cm^{-1} Oe^{-1} at $f = 0.06$ which is less than half with those obtained for the PZT/ferrite ceramic composite (115 mV cm^{-1} Oe^{-1}).[105] Since this ME response is mainly determined by the $f_{\text{Terfenol-D}}$, the pre-treatment of the Terfenol-D nanoparticles, by the use of surfactants can change the ME coupling.. Surfactants are usually used in such a way to improve dispersibility and dispersion stability of nanoparticles[106,107] in different kind of matrices. In the case of the PZT/ferrite ceramic composite, surfactants increase the percolation threshold. This experimental change has two consequences:

i) the maximum magnetostrictive filler concentration allowed in the ME nanocomposites is increased;
ii) a soft and inactive interfacial layer is induced in the Terfenol-D nanoparticles.

Although the first consequence is extremely positive since it allows higher magnetostrictive content in the ME composite, the second produces a negative effect on both the piezo and ME response of the nanocomposites as already discussed in this Feature Article.[62] Further improvement in the ME response of this MF composite lies in increasing the $f_{\text{Terfenol-D}}$ and simultaneously ensuring good interfacial contact between phases by optimization the nanocomposite processing. In view of this fact, theoretical calculations were performed on the mechanical boundary conditions influence in the ME properties based on the Green's function technique.[98,108] Three different mechanical boundary conditions were considered:

i) completely mechanical clamped boundary condition;
ii) completely mechanical free boundary condition;
iii) completely mechanical clamped in the *zz* direction and free in the transverse direction.

For the composite with $f = 0.06$, the maximum α_{33} values are 117, 362, and 62 mV cm^{-1} Oe^{-1} for situations i), ii) and iii), respectively. The same calculations also revealed that the PZT particles polarization and the inactive PZT/PVDF interface have a significant effect on the ME properties of the nanocomposites. Random orientations of the polarization in the PZT particles result in the disappearance of piezoelectricity in the composites, and thereby the disappearance of the extrinsic ME effect. Although the thin interfacial layer with the same elastic constants as the polymer matrix has only a slight effect on the effective magnetostriction of the composites, the piezoelectric effect is strongly influenced by the interfacial layer surrounding the PZT particles.[64]

The influence of different polymers in the ME response of the same kind of MF nanocomposites was recently investigated.[109] Polymer electrolyte polyethylene (PEO) and lithium perchlorate-doped PEO, lithium perchlorate-doped PEO (Li$^+$-PEO) and poly(methyl methacrylate) (PMMA) were mixed separately with Terfenol-D and PZT particles aiming to evaluate the significance of the polymer matrix conductivity in the ME response of the samples. The obtained α_{31} were 1.3, 3.2, and 4.8 mV cm^{-1} Oe^{-1}, respectively, for the Li$^+$-PEO, PEO and PMMA polymer matrix. Those results confirm that samples with higher conductivity exhibit lower ME responses.[72]

Although the flexibility, structure, simple fabrication, and easy shaping of the polymer as a binder ME materials provide attractive advantages in possible ME applications, these added features are limited since all of them are inferior to those of the particulate nanocomposites.

2.4. Laminated Composites

In the three-phase Terfenol-D/PZT/PVDF particulate composites of the previous section, the $f_{\text{Terfenol-D}}$ allowed in the nanocomposites is quite low, which strongly limits the ME response of the MF nacomposites. To eliminate this limitation, a different class of ME material has been developed: laminated composites.

A laminate bilayer or multilayer configuration for ME composites has other advantages over bulk nanocomposites. In particular, the loss of polarization in bulk composites due to leakage currents can be overcome in layered structures. The piezoelectric phase can be poled to enhance the ME coupling and it is also possible to vary the poling and applied field directions to achieve maximum ME coupling.

MF laminated composites consisting on one Terfenol-D/PVDF particulate composite layer sandwiched between two PZT/PVDF particulate layers prepared by hot-molding technique has been reported.[80] The polymer phase PVDF is used just as a binder, with no influence on the ME properties of the laminated composite. Experiments show that with $f_{\text{PVDF}} \leq 0.3$, the low concentration of PVDF leads to low quality of the composites as the connection between the three phases is poor, leading to low ME performance. The ME properties are improved in the intermediate f_{PVDF} concentration range ($0.3 \leq f_{\text{PVDF}} \leq 0.5$) and as f_{PVDF} further increases ($f_{\text{PVDF}}>0.5$), the high concentration of inert PVDF causes weak dielectric, magnetostrictive, piezo and ME activity of the three-phase laminated Terfenol-D/PZT/PVDF composites. A maximum value for α_{33} of 80 mV cm^{-1} Oe^{-1} was obtained at 1 kHz, 4 kOe, and $f_{\text{PVDF}} = 0.5$. The maximum ME sensivity of such laminated composites can reach up to 3 V cm^{-1} Oe^{-1} at a resonance frequency of around 100 kHz.[110] The difference in the longitudinal (α_{33}) and transversal (α_{31}) ME sensitivity, 3 and 3.8 V cm^{-1} Oe^{-1}, respectively, is fully attributed to the anisotropy of the laminated ME samples. At high bias, magnetostriction becomes saturated faster under in-plane bias than in out-of-plane bias producing a nearly constant electric field in the PZT, thereby decreasing α_{31} with increasing bias.

Novel laminated conformations of the ME samples, consisting on a PZT/PVDF particulate layer sandwiched between two Terfenol-D/PVDF particulate composite layers[111] were investigated. With this conformation, the maximum ME sensitivity α_{33} was improved to 300 mV cm^{-1} Oe^{-1} at a frequency below 50 kHz and about 6 V cm^{-1} Oe^{-1} at the resonance frequency of around 80 kHz. The ME response of such composites is also strongly dependent on the applied bias and on the thickness ratio (t_p/L) between the Terfenol-D/PVDF layers and the PZT/PVDF layer. Keeping the thickness of the composite (L) equal to ≈2.5 mm, the t_p/L ratio was varied from 1/7 to 5/7 by increasing the thickness of the PZT/PVDF particulate layer (t_p) The α values of the composites first increase with t_p/L until a 2/7 ratio, which could be attributed to the increase in the effective piezoelectric effect. However, with further increasing t_p/L, the ME sensitivity declines after a maximum value, which is due to the reduction in magnetostrictively induced strain of the laminated composites with increasing t_p/L.[79]

Finally, three-phase Terfenol-D/PZT/binder composites were fabricated by substituting PVDF by Spurr epoxy (Polysciences Inc., USA).[112] The ME properties of such materials were investigated experimentally and theoretically confirmed by the use of the equivalent circuit approach.[113] Samples with a $f_{\text{Terfenol-D}} = 0.5$ in the Terfenol-D/Spurr epoxy laminates with two different PZT concentrations ($f_{\text{PZT}} = 0.6$ and $f_{\text{PZT}} = 0.75$) in the PZT/Spurr epoxy laminate were measured. At a frequency of 10 kHz and 504 Oe field, the obtained value for α_{31} was ~0.3 and 0.4 V cm^{-1} Oe^{-1}, respectively for the $f_{\text{PZT}} = 0.6$ and $f_{\text{PZT}} = 0.75$ samples. When the frequency was changed to the resonance (≈55 kHz), α increases up to 10 V cm^{-1} Oe^{-1} in the case of the $f_{\text{PZT}} = 0.6$ and 11 V cm^{-1} Oe^{-1} in the case of the $f_{\text{PZT}} = 0.75$ composite. The increase of α with increasing f_{PZT} is expected, due to the increase of the piezoelectric phase. It is nevertheless to notice that the improvement of the ME response is accompanied by a decrease of the flexibility and strength of the composite.

A similar ME composite concept uses PU to increase the ME coupling between the piezoelectric PVDF and the magnetostrictive material (Fe_3O_4 and Terfenol-D).[114] It was reported a ME in bi and trilayered composites consisting in on layer PVDF and one or two layers of PE filled with Fe_3O_4 or Terfenol-D particles, modeled by a driven damped oscillation system,[115,116] with a highest α_{33} obtained for the trilayered sample of PE + 2 wt% Fe_3O_4/PVDF/PE+2 wt% Fe_3O_4 with a value of 753 mV cm^{-1} Oe^{-1} at −2000 Oe.

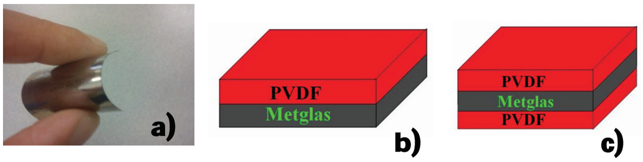

Figure 5. a) Picture of a flexible PVDF/Metglas unimorph laminate; b) unimorph configuration, and c) three layer laminate. (Panels (b) and (c) are based on the experimental description reported in ref. [73]).

Further, ME laminates of vinyl ester resin (VER)-bonded Terfenol-D magnetostrictive layer ($f_{\text{Terfenol-D}}$ from 0.16 to 0.48) and a PZT piezoelectric layer glued together with a conductive epoxy,[117] show α_{31} values increasing gradually with increasing $f_{\text{Terfenol-D}}$ in the MS layer reaching a saturation for $f_{\text{Terfenol-D}} > 0.4$ due to the increasing elastic modulus and piezomagnetic coefficient of the magnetostrictive phase. A maximum value of 2.7 V cm^{-1} Oe^{-1} was obtained at 666 Oe DC field with $f_{\text{Terfenol-D}}$ in the magnetostrictive layer equal to 0.48.

A bilayer disk prepared by bonding a PZT disk with Terfenol-D/low viscosity epoxy disk[118] show at a bias of 3 kOe three resonance peaks with α_{33} values of 2.79 V cm $^{-1}$ Oe^{-1} at 35 kHz, 0.924 V cm^{-1} Oe^{-1} at 100 kHz and 1.31 V cm^{-1} Oe^{-1} at 122 kHz respectively.[119] The resonance peak at 122 kHz is attributed to the transversal resonance,[120,121] which is present in many sandwich laminated composites.[80,122] The observation of three ME resonance peaks in laminated composites is for the first time reported in this work.

Thin, flexible ME laminates (**Figure 5**a) composites were fabricated following similar approaches but with different magnetostrictive layers, as for example, Metglas/PVDF unimorph (Figure 5b) and threelayer (Figure 5c) sandwich configurations.[73]

Those laminates required an applied H_{DC} of only 8 Oe in order to achieve a maximum ME response, 1/50th of that required for the previous ME laminates. These small magnetic field ME laminates have giant ME voltage coefficients and excellent sensitivity to small variations in both AC and DC magnetic fields. The Metglas layer and PVDF layers are glued together using an epoxy and both laminate types were found to have a strong ME enhancement: three-layer composites: α_{31} = 238 V cm^{-1} Oe^{-1}; unimorph composites: α_{31} = 310 V cm^{-1} Oe^{-1}, both near the longitudinal resonance frequency at 50 kHz. At lower frequencies, a maximum value of 7.2 V cm^{-1} Oe^{-1} was obtained for both geometries. Although the magnetostriction of Metglas SA1 was only 42 ppm which is far smaller than the giant magnetostriction of Terfenol-D, the maximum value of its effective piezomagnetic coefficient $d_{33\text{m}} = 4 \times 10^{-6}$ Oe^{-1} is three to four times larger than the one for Terfenol-D $d_{33\text{m}} = 1.2 \times 10^{-6}$ Oe^{-1} due to the small saturation field.[123] This extremely low H_{DC} requirement is an important advantage of Metglas/PVDF laminates over other previously reported types, offering potential in practical applications.

After the first works on Metglas/PVDF laminate nanocomposites,[73] several works were devoted to these promising ME material. For example, taking advantage of the magnetic flux concentration effect of Metglas as a function of its sheet aspect ratio values of α_{31} = 21.46 V cm^{-1} Oe^{-1} were obtained in a PVDF/Metglas 2605SA1 laminate a composite at a non resonance frequency of 20 Hz and at 3 Oe DC magnetic field.[74]

By taking advantage of the anisotropy of PVDF/Metglas-SA1-MP4010XGDC laminates it was demonstrated the ability of such composites to be used as an ultra-sensitivity detection device of weak H_{DC} (1×10^{-9} Oe).[9] This high sensitivity is due to the:

i) large piezoelectric voltage coefficient of PVDF that indicates a high output voltage in response to a small variation of strain;
ii) high piezomagnetic coefficient of the Metglas-SA1-MP4010XGDC alloy;
iii) relatively small demagnetization factor of the Metglas-SA1-MP4010XGDC alloy.

Since α is proportional to the piezomagnetic and piezoelectric voltage coefficients and inversely proportional to the demagnetization factor, a high sensitivity is characteristic of the Metglas/PVDF composites. The maximum α_{31} value obtained in the PVDF/Metglas-SA1-MP4010XGDC laminate was 400 mV cm^{-1} Oe^{-1} at 1 kHz frequency and H_{DC} = 3 Oe.

Further, as it was found that the depolarization effect is prone to occur in polymers such as PVDF, the effect of two types of poling processes were investigated in the ME properties of PVDF hexafluoropropylene (PVDF-HPFP)/Metglas laminates.[76] After applying the so-called "conventional poling", usually used in the poling of piezoelectric polymers[124] or "cycling poling".[125] In the first, a D.C. electric field ranging from 100 to 300 MV/m was applied to the sample during 300 s at room temperature. Regarding the second poling method, starting at low electric fields, the sample is cycled through many "loops" until a consistent behavior is indicated. Higher fields are then utilized until the desired stable polarization is achieved. Comparing both methods, it was verified a shift of the ME peak (α vs DC magnetic field) of one method with respect to the other, attributed to the variation of the boundary conditions of the magnetostriction of the Metglas. Since the maximum peak is related to the piezomagnetic coefficient of Metglas, the variation of magnetostrictive vibration will result in the variation of the magnetostrictive coefficient as well in a shift of the piezomagnetic coefficient peak. In this case, variation in the maximum of the α values with different poling processes is due to the fact that conventional poling uses DC electric field, while cyclic poling employs an AC electric field, which produces different orientation stresses in the dielectric polymer. The highest α_{31} obtained was 12 V cm^{-1} Oe^{-1} at 5 Oe and is lower than the values obtained for the previously discussed PVDF/Metglas laminates, however it has the advantage of allowing the change of the magnetic DC field at witch is obtained through modifications in the poling process (electric field strength and type of poling).

A novel approach to high performance ME polymer composites was presented with the chain-end cross-linked ferroelectric P(VDF-TrFE)/Metglas 2605 SA1 composites.[126] The performance improvement is due to the introduction of chain-end cross-linking and polysilsesquioxane structures into the P(VDF-TrFE) matrix which leads to the formation of larger crystalline samples and consequently better piezoelectric response in comparison to those of pristine P(VDF-TrFE) copolymers. With better piezoelectric properties a higher α is expected. For the cross-linked P(VDF-TrFE)/Metglas laminate an α_{31} value of 17.7 V cm^{-1} Oe^{-1}

Table 2. Comparison of the main characteristics of the developed polymer-based magnetoelectric materials.

Type	Constitution	$H_{\text{DC-Max. ME}}$ [Oe]	Ref.	α [mV cm^{-1} Oe^{-1}]	$\alpha_{\text{resonance}}$ [mV cm^{-1} Oe^{-1}]
Nanocomposite	PE/Fe_3O_4	0	[92]	11.4	–
	PE/Nickel	0	[92]	6	–
	P(VDF-TrFE)/$Ni_{0.5}Zn_{0.5}Fe_2O_4$	5000	[50]	0.1	1.35
	P(VDF-TrFE)/$CoFe_2O_4$	2500	[42]	4.1	41.3
	P(VDF-TrFE)/$CoFe_2O_4$	2000	[51]	–	40
Polymer as a binder composites	PVDF/Terfenol-D/PZT	2000	[72]	42	–
	PEO/Terfenol-D/PZT	1400	[109]	1.3	–
	Li^+-PEO/Terfenol-D/PZT			3.2	–
	PMMA/Terfenol-D/PZT			4.8	–
Laminate	PVDF/Terfenol-D/PZT	4000	[110]	80	3000
	PVDF/Terfenol-D/PZT	4000	[111]	300	6000
	Spurr epoxy/Terfenol-D/PZT	504	[113]	400	1100
	PE/PVDF/Fe_3O_4	2000	[114]	753	–
	VER/Terfenol-D/PZT	666	[117]	2700	–
	PZT/Terfenol-D/epoxy	3000	[119]	1310	2790
	Gd crystal/P(VDF-TrFE)/silver conductive epoxy	200	[131]	500	–
	PVDF/Metglas unimorph	8	[73]	7200	238000
	PVDF/Metglas three-layer				310000
	PVDF/Metglas	8	[74]	21460	–
	PVDF/Metglas	3	[9]	400	–
	PVDF-HPFP/Metglas	5	[76]	12000	–
	Cross-linked P(VDF-TrFE)/Metglas 2605	4	[126]	17700	383000
	PVDF/$Ni_{50}Mn_{29}Ga_{21}$	5100	[75]	1240	–

was achieved under a DC magnetic field of 3.79 Oe at 20 Hz, whereas the value obtained for the pristine P(VDF-TrFE)/Metglas under the same conditions is α_{31} = 6.9 V cm^{-1} Oe^{-1}. The α_{31} values for cross-linked P(VDF-TrFE)/Metglas laminates can be further improved to 383 V cm^{-1} Oe^{-1} at a resonance frequency of 65 kHz. The later laminate composite not only shows the largest value of α in polymer-based ME materials but also points to a way to improve the piezoelectric properties of the piezoelectric layer and hence the ME response.

Leaving behind the ME PVDF based/Metglas composites, this laminated polymeric ME materials section is concluded with the large ME response from mechanically mediated magnetic field-induced strain effect in a PVDF/$Ni_{50}Mn_{29}Ga_{21}$ single crystal.[75] $Ni_{50}Mn_{29}Ga_{21}$ single crystal shows giant DC magnetic field induced strains of 6–10% in the tetragonal and orthorhombic martensitic phases, which has attracted interest for ME applications.[127] Showing obvious differences from the traditional magnetostrictive phases (Terfenol-D, ferrites or Metglas), the mechanism of the giant magnetic field-induced strains is due to the reorientation of the martensitic twin variants under an applied magnetic field as a result of magnetocrystalline anisotropy.[128,129]

PVDF/$Ni_{50}Mn_{29}Ga_{21}$ single crystal bilayered composites were produced by adhering one layer of the ferromagnetic shape memory alloy to one layer of the piezoelectric polymer with a conductive silver epoxy. The largest value α_{33} of 1.24 V cm^{-1} Oe^{-1} obtained at 1 kHz and at an optimal magnetic field of 5.1 kOe was experimentally and theoretically confirmed.[28,130] This investigation not only reported a different constitution in ME laminates but also created a distinct physical mechanism for realizing such effect. An alternative concept in ME polymer laminated composites is based on thermal mediation.[131] This kind of MF material uses the large magnetocaloric effect (MCE), i.e., a temperature change induced in the ferromagnetic Gd crystal by a magnetic field and a large pyroelectric response in the ferroelectric P(VDF-TrFE) (68/32 mol%). Composites were prepared by bonding a Gd crystal plate to the P(VDF-TrFE) with a silver conductive adhesive epoxy to ensure a good thermal contact between the layers. An α value of 0.5 V cm^{-1} Oe^{-1} was obtained at 293 K in an AC field of 2.4 Hz and 120 Oe amplitude. The α was further enhanced to 0.9 V cm^{-1} Oe^{-1} by exploiting the magnetic flux concentration effect.[132]

As a conclusion from this section, the results obtained for the main polymer-based ME material are shown in **Table 2** ordered by composite type.

3. Applications

Based on the previous sections it is concluded that ME materials in general and polymer-based ME materials in particular are ready for technological applications. Promising applications include magnetic field sensors, transducers, filters, oscillators, phase shifters, memory devices, and biomedical materials, among others.[5,13] In some of these applications polymeric based ME materials, due to the polymers unique characteristics such as flexibility, lightweight, versatility, low cost and in some cases biocompatibility can be taken to advantage. Some of these applications are highlighted as follows.

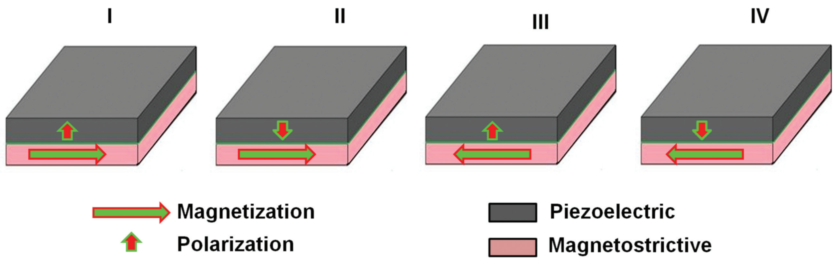

Figure 6. Representation of a four states memory based on ME materials.

3.1. Four State-Memory

To meet the intense demand of multimedia storage many efforts are being made to develop storage technologies with higher storage speed and density.[133,134] In the traditional two state (0 and 1) memories, the memory element is a magnetic tunnel junction that consists on an insulating tunnel barrier sandwiched by two magnetic electrodes.[135] The resistance of such junctions strongly depends on the relative orientation of the magnetic moments, which is used to determine the memory state (0 or 1) from the two magnetic electrodes.[136] The coded magnetic bits can then be read out nondestructively by detecting such resistance changes, however, in the writing process, the magnetic bits are usually encoded by the use of high magnetic fields which is a process relatively slow and energetically expensive.[3] These problems can be solved with the manipulation of the magnetization direction by the use of an electric field,[137] taking advantage of the ME effect.[58,138] For this kind of multi-state memory (**Figure 6**) the multiferroicity is the essential factor for the information storage while the ME or the magnetodielectric effect[139] is the mechanism for the reading and writing procedure.[140]

A four-state memory cell based on the ME PZT/Co bilayer composite[140] has been already proposed. Co was used since it is widely used in magnetic recording and PZT due to its ferroelectric properties. The composite was obtained by gluing one layer of PZT to one layer of Co with an epoxy. The polarization/magnetization of such composite can be controlled by the application of magnetic and electric fields and the combination of the remnant ferroelectric polarization and magnetization in the PZT/Co bilayer memory cell exhibits the desired four physical states. Results gave clear four-state signals of 15.8, –4.4, 5.5, and –11.3 μV, which demonstrated the feasibility of the design.

A distinct room temperature ME memory was presented in ref. [141] in which a magnetoelastic nanostructured multilayer ($TbCo_2$(5 nm)/FeCo(5 nm)) with the required uni-axial characteristic was deposited onto a commercial piezoelectric actuator (from Piezomechanik Gmbh.). As a result of the inverse magnetostrictive effect, the effective anisotropy of the magnetic element was controlled by the applied voltage and used to switch magnetization from one state to the other.

A positive voltage sets the magnetization in one of the stable positions, whereas a negative voltage sets it in the other position. The position is kept when no voltage is applied. Since the information is stored magnetically, the readout can be made using magnetoresistive techniques. Theoretical calculations[142] have confirmed that the properties of existing materials were compatible with the realization of such a device at the nanometer scale. With the reduction of size, densities up to 40 Gbits cm^2 per layer can be expected for low energy, nonvolatile memory devices. Given the very low expected power, such a device is a strong contender for vertical integration of several layers, quickly increasing the memory density.[141,142]

As the current electronic market demands are intimately related to the use of flexible materials,[143] not only the magnetic/dielectric properties of materials will play a key role in the future but also their mechanical properties.[144] In this way, the substitution of PZT by a polymer in bilayer four-state ME memories will meet these new challenges. Contrary to what happened a few decades ago, when polymers were just used as a binder in memory devices,[145,146] devices based on polymeric materials are now a interesting topic due to their simplicity, good scability, low-cost, 3D stacking capability, and large capacity for data-storage.[147] These electroactive polymers are usually deposited by ink-jet printing, spin-coating, or vacuum evaporation on a variety of substrates for the fabrication of memories.[148] In this way, polymers, may also acquire in the near future a more central status in the memory market due to the polymeric four-state ME memory devices.

Since static magnetic and electric fields are used for writing information in the four-state ME memories and the ME coefficient is used for reading with the help of a small bias magnetic field, such coefficient is determining in the practical applicability of this new kind of memories. It was already reported in the literature that materials with ME coefficients in the order of 30 mV cm^{-1} Oe^{-1} can be used as components of room temperature four-state memory prototypes.[149] Accordingly, and after a detailed analysis of the ME coefficients obtained from the different approaches for preparing polymer-based ME composites summarized in Figure 9, it is possible to verify that almost all of them can be used in the development of this kind of multi-state memory.

3.2. Energy Harvesting

The ever decreasing power requirement of electronic sensors and devices[150] has attracted attention to energy harvesting technologies.[151] In particular, there has been significant interest in the area of the vibration energy based on piezoelectric and magnetic harvesters.[152–155] After the first hypothesis of ME materials as energy harvesting devices[156] some studies have been reported in this area. As described in the previous section, there have been significant advances made in improving the

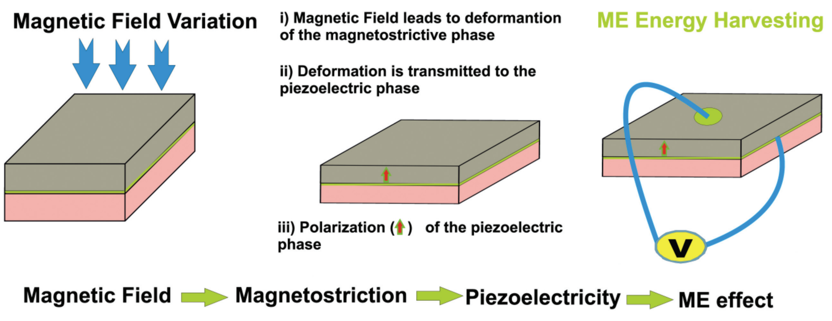

Figure 7. Representation of the ME energy harvesting mechanism.

magnitude of the ME coefficient of laminate composites, which will improve the ME energy harvesting efficiency (**Figure 7**). A combined magnetic and vibration energy harvesting device may be implemented on silicon using the thin film deposition methods and fabrication process flow and combination with the micro-machining technique.[157]

The energy harvesting in the Terfenol-D/PZT/Terfenol-D laminate composites has been reported to provide an energy density of 2.0 mW per cubic inch with vibrations of 21 Hz and 100 mg.[158] Furthermore, a windmill based on this approach is under development.[159] Ceramic based laminates energy harvesting materials constituted by PZT/$CoFe_2O_4$ and PZT/Terfenol-D have been also reported.[160–162] In the case of the PZT/$CoFe_2O_4$ energy harvester, magnetically forced extensional vibrations of laminated plates with piezoelectric and piezomagnetic layers were theoretically analyzed. It was shown that such a structure can be used to harvest magnetic energy and convert it to electric energy. The theoretical ME coefficient reported for the PZT/$CoFe_2O_4$ energy harvester was 2.5 V Oe^{-1}.

In more experimental work, ME PZT/Terfenol-D laminates were placed between an oscillating spherical steel bearing and a rare-earth magnet (NdFeB) to produce a peak rms power of 121 μW from an rms host acceleration of 61 mG at 9.8 Hz.[162] This approach may be useful in the future for kinetic energy harvesting for applications where the host accelerations are multiaxial.

An electromagnetic energy harvesting scheme by using the PZT/Terfenol-D transducer and a power management circuit was presented in ref. [161]. In such a transducer, the vibrating wave induced from the magnetostrictive Terfenol-D in the dynamic magnetic field converges using a Be–bronze ultrasonic horn. Consequently, more vibrating energy can be converted into electricity by the PZT. A switching capacitor network for storing electricity was also reported. The output of the transducer charged the storage capacitors in parallel until the voltage across the capacitors reached a threshold, and then the capacitors were automatically switched to being in series. In this way, more capacitors can be employed in the capacitor network to further raise the output voltage in discharging. For the weak magnetic field environment, an active magnetic generator and a magnetic underground coil antenna were used for producing an ac magnetic field of 0.2–1 Oe at a distance of 25–50 m. In combination with the supply management circuit, the electromagnetic energy harvester under an AC magnetic field of 1 Oe can supply power for wireless sensor nodes with power consumption of 75 mW for a duration of 620 ms.

Despite all these developments, the next generation of energy-harvesting applications, such as wearable energy-harvesting systems, may require the piezoelectric materials to be flexible, lightweight, and even biocompatible.[163] In this way, ME materials based on piezoelectric polymers may be an interesting approach to meeting these requirements due to their flexibility, versatility, and low cost.[164] Some of the above reported ME coefficients on polymer-based ME materials are of the same order of magnitude as the best ones obtained in the ME materials that are already being used/investigated as energy harvesters, and this will encourage the emergence of the next generation of polymer-based ME energy-harvesting materials.

3.3. Magnetic Field Sensors

Magnetic sensors have been in use for well over 2000 years. Early applications were for direction finding in navigation.[165] Today, magnetic sensors are also used in navigation but many more uses have evolved. The technology for sensing magnetic fields has also evolved driven by the need for improved sensitivity, smaller size, and compatibility with electronic systems.[166] Traditional magnetic sensors like Hall or magnetoresistive sensors need power supply, which raises some limitations. In this context, self-powered magnetic field sensors that directly transfer magnetic energy into electric signals are of large interest and can be realized thanks to the ME effect (**Figure 8**).[167]

Following the suggestion by Nan et al.[63] to use ferroelectric polymers/rare-earth–iron alloys composites, such as magnetic ME sensors in radioelectronics, optoelectronics, and microwave electronics and transducers, magnetoelectric bulk composites containing 95 wt% of yttrium-iron garnet and 5 wt% of lead PZT and multilayer composite material consisting of PZT and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ were used for sensor applications.[168] The ME sensor comprised a disk or plate from the magnetoelectric material with two electrodes for connecting to the voltage meter. This was followed by numerous reports about PZT based magnetic ME sensors;[167–172] vortex magnetic field sensor based ring-type PZT/Terfenol-D sensors,[170] PZT/$(Fe_{80}Co_{20})_{78}Si_{12}B_{10}$ laminates ME sensor for microtesla sensitivity [167] and the effect of the

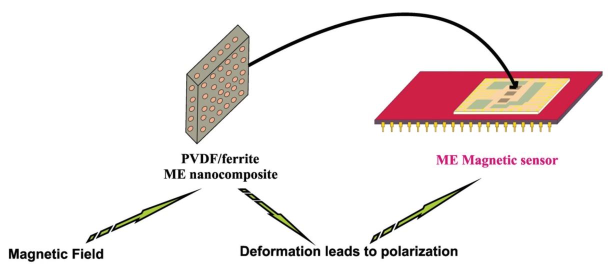

Figure 8. Representation of the ME magnetic field sensing mechanism.

mutual inductance on the magnetic field sensitivity of the ME PZT/Metglas laminate,[172] respectively.

The low flexibility, cost, and fragility of PZTs[173,174] do not meet the challenges of future sensor applications,[175,176] therefore multiferroic and ME polymer-based composites are possible successful alternatives for the more traditional ceramic based ME magnetic sensors.[42,44,50] In this way, the ME laminates of Metglas/PVDF magnetic field sensors were experimentally studied in ref. [177] and the performance was compared to the prediction from a theoretical analysis. The field sensitivity and signal-to-noise ratio (SNR) of ME laminates were also investigated. The results indicate that increasing the electrode area (number of layers) of PVDF can enhanced the field sensitivity and SNR. This work has introduced a figure of merit to characterize the overall influence of the piezolayer properties on the SNR and has shown that newly developed piezoelectric single crystals of PMN-PT and PZN-PT have potential to reach very high SNR for ME magnetic sensors. The results also show that the ME coefficients which are presently used to compare the ME materials developed may not be relevant when using these ME materials for magnetic sensors.

This new kind of ME magnetic sensors also have enormous potential as by-products related to magnetic sensors: electric current sensors, speed sensors, angular sensors, electronic steering, throttle control, battery management, vehicle transmission, digital compasses, and GPS devices[165] are just some examples and many of them are already being studied.[170,178,179]

4. Conclusions

In conclusion, polymer-based ME materials are a promising research field with large interest for applications that certainly will appear soon. The results obtained from the different approaches for preparing such composites are presented in Table 2 and summarized in **Figure 9**. The obtained values of the magnetoelectric coefficients as well as the broad range of the magnetic field at which they respond, together with the flexibility, robustness and ease of fabrication related to the polymer-based materials, allow a large range of applications, in particular in the fields of sensors and actuators.

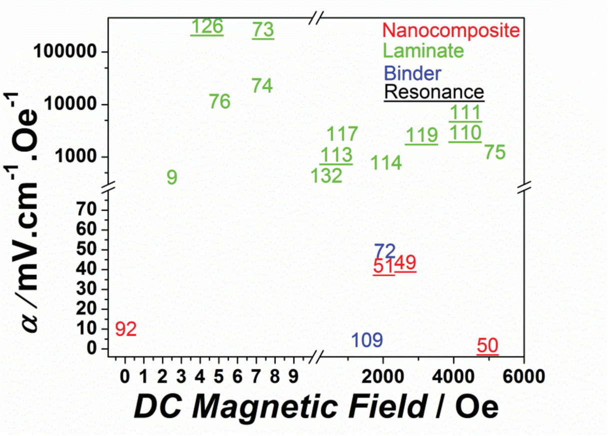

Figure 9. Distribution of the maximum polymer-based magnetoelectric coefficient (α) by reference, type and DC magnetic Field at α maximum.

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