Proceedings of the 3rd International Conference on Materials Chemistry and Environmental Engineering (CONF-MCEE 2023), Part II
DOI: 10.54254/2755-2721/7/20230431

Effective design of advanced flexible piezoelectric materials

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Abstract. Piezoelectric ceramics are relatively common materials that can convert mechanical energy and electrical energy into each other. They are widely used in our life in electroacoustic devices, communication, navigation, precision measurement and ultrasonic energy conversion. Its texture is hard and brittle, its processability is not very good, and its use is limited. If piezoelectric ceramics are made into flexible piezoelectric composites by compounding with flexible matrices to improve mechanical properties, they can be applied to wearable and flexible devices. This paper briefly introduces the basic principle of the piezoelectric effect, introduces the preparation methods of three typical flexible piezoelectric composites and their dielectric, piezoelectric and mechanical properties, introduces the recent research work and the latest scientific research achievements of relevant teams, summarizes the research progress of flexible piezoelectric materials, and provides ideas for finding flexible piezoelectric composites that have good dielectric, piezoelectric and mechanical properties.

Keywords: piezoelectric ceramics, flexible materials, composites.

1. Introduction

Piezoelectric ceramics are a kind of material with a piezoelectric effect. In 1880, J Curie and P Curie found that positive piezoelectric effect, that is, some crystals are deformed by applying mechanical stress in a certain direction, which causes the relative displacement of the centers of gravity of positive and negative charges in the dielectric body and polarization, and generates bound charges with equal numbers and opposite signs on the surface. The density of bound charges is proportional to the applied stress. After that, they experimentally confirmed the inverse piezoelectric effect [1]. That is, when an electric field is applied to the crystal in a certain direction, the center of gravity of positive and negative charges in the medium is displaced by the electric field, and deformation will occur, which is proportional to the strength of the electric field.

The essence of the piezoelectric effect is the polarization of the crystal medium. When some non-centrosymmetric crystals receive an external force, the centers of gravity of positive and negative charges will shift relatively, and the electric dipole moment will be generated in the unit cell. The crystals show polarity externally. A crystal with a symmetric center does not have piezoelectricity because its central symmetric arrangement will not be damaged by deformation, and the gravity centers of positive and negative charges cannot be displaced by mechanical force alone. The mutual transformation of mechanical and electrical energy can be realized through the piezoelectric effect, so piezoelectric

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ceramics are widely used in electroacoustic devices, communication, navigation, precision measurement, ultrasonic energy conversion and other fields in our lives [2].

2. Performance parameters of piezoelectric materials

2.1. Dielectric constant

Permittivity is a characteristic parameter of dielectrics, reflecting the materials' ability to retain a charge. The dielectric constant ϵ of the material can be measured by a parallel plate capacitor.

$$\epsilon = \frac{Cd}{A} \tag{1}$$

wherein C is the capacitance, d is the distance between the electrode plates, and A is the area of the electrode plates.

In practical research, relative permittivity ϵ_r is usually used, which is defined as the ratio of the dielectric constant of the material ϵ to the dielectric constant of the vacuum ϵ_0:

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} \tag{2}$$

wherein vacuum dielectric constant $\epsilon_0 = 8.854 \times 10^{-12}$ F/m

2.2. Dielectric loss

The dielectric constant is related to the electric field's temperature and frequency. Different from the static dielectric constant under a constant electric field, the complex dielectric coefficient of the material can be measured under an alternating electric field. Apply alternating voltage $U = U_0 e^{i\omega t}$ to the parallel plate capacitor. If the material is a non-polar dielectric with ideal insulation, then the charge on the plate $Q = CU$, and the current on the external circuit:

$$I = \frac{dQ}{dt} = i\omega C U_0 e^{i\omega t} = i\omega CU \tag{3}$$

The phase difference between current and voltage is 90°.

If it is a non-ideal capacitor, due to the conductance component GU, the current $I = (i\omega C + G)U$, the phase difference between current and voltage is not 90° (Figure 1).

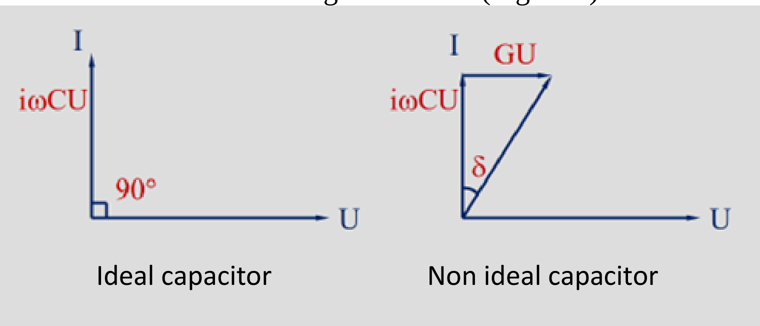

Figure 1. Phase difference between current and voltage.

Wherein δ is the loss angle. From the current $I = (i\omega C + G)U$, the conductance $G = \sigma A/d$ and the capacitance $C = \epsilon A/d$, the current density J is obtained:

$$J = (i\omega\epsilon + \sigma)E \tag{4}$$

And from $J = \sigma E$ lead out complex conductivity σ' :

$$\sigma' = \sigma + i\omega\epsilon \tag{5}$$

Defining complex permittivity ϵ' from $J = i\omega\epsilon E$:

$$\epsilon' = \frac{\sigma'}{i\omega} = \epsilon - i\frac{\sigma}{\omega} \tag{6}$$

Generally, the size of the dielectric constant is represented by the real part, and the dielectric loss is represented by the ratio of the imaginary part to the real part, that is, the tangent value of the loss angle $\tan\delta$.

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2.3. Piezoelectric constant

The piezoelectric constant is a proportional constant that can directly represent the piezoelectric properties of materials. Measuring the piezoelectric constant of materials is the main means to characterize the piezoelectric properties of materials. Different expressions of piezoelectric constants can be obtained by measuring piezoelectric properties from different angles.

The ratio of strain change to electric field strength change under constant stress or the ratio of potential shift change to stress change under constant electric field is called piezoelectric strain constant d (i, j indicates direction).

$$d_{ij} = \left(\frac{\partial S_j}{\partial E_i}\right)_T = \left(\frac{\partial D_i}{\partial T_j}\right)_E \tag{7}$$

The ratio of stress change to electric field strength change under constant strain or the ratio of potential shift change to strain change under constant electric field is called piezoelectric stress constant e.

$$e_{ij} = \left(-\frac{\partial T_j}{\partial E_i}\right)_S = \left(\frac{\partial D_i}{\partial S_j}\right)_E \tag{8}$$

The ratio of the change of electric field strength to the change of stress under the action of constant potential shift or the ratio of the change of strain to the change of potential shift under the action of constant stress is called piezoelectric voltage constant g.

$$g_{ij} = \left(-\frac{\partial E_i}{\partial T_j}\right)_D = \left(\frac{\partial S_j}{\partial D_i}\right)_T \tag{9}$$

The ratio of stress change to potential shift change under constant strain or the ratio of electric field strength change to strain change under constant potential shift is called piezoelectric stiffness constant h.

$$h_{ij} = \left(-\frac{\partial T_j}{\partial D_i}\right)_S = \left(\frac{\partial E_i}{\partial S_j}\right)_D \tag{10}$$

The most commonly used piezoelectric constant is d_{33}, and the larger the value, the better the piezoelectric property of the material.

2.4. Lead-free piezoelectric ceramics

At present, the commonly used piezoelectric ceramics are mainly lead-containing systems. These ceramic materials contain about 60 % PbO or Pb_3O_4 [3]. The human body's toxicity and the natural environment's harm cannot be ignored. Therefore, the research and development of lead-free piezoelectric ceramics have become an inevitable trend.

The main research objects of lead-free piezoelectric ceramics are potassium sodium niobate-based (KNN), bismuth sodium titanate-based (BNT) and barium titanate-based (BT) ceramics [4]. KNN-based piezoelectric ceramics can be used in a wide range of temperatures due to their excellent piezoelectric properties and high Curie temperature, and their low cost is conducive to industrialization [5]. It is one of the material systems expected to replace lead-based piezoelectric ceramics [6].

2.5. Piezoelectric composite

Compounding is a major development trend of new piezoelectric materials [7]. Using different reinforcing materials to composite with the matrix can keep the characteristics of the original component materials, make the components cooperate and complement each other, and obtain more complex and superior comprehensive properties [8]. For piezoelectric ceramics, the application is limited by its poor mechanical properties. Its brittleness can be significantly reduced through flexible composite materials, its toughness and ductility can be increased, and its machinability can be improved so that it can be widely used in wearable devices and flexible electronic components.

Piezoelectric composites can be classified into ten types according to the connectivity of piezoelectric ceramic components and matrix components, namely 0-0, 0-1, 0-2, 0-3, 1-1, 1-2, 1-3, 2-2, 2-3, and 3-3 types [9]. The two numbers refer to the connectivity of the ceramic phase and the matrix, respectively. 0 indicates that it exists in the form of particles [10]. 1, 2 and 3 indicate one-dimensional, two-dimensional and three-dimensional connected structures. At present, there are two types of piezoelectric composites:

One is the 0-3 type obtained by directly adding ceramic material particles into the flexible matrix (Figure 2). The molding process is simple, the mechanical properties are good, and the dielectric and piezoelectric properties are insufficient [10-13].

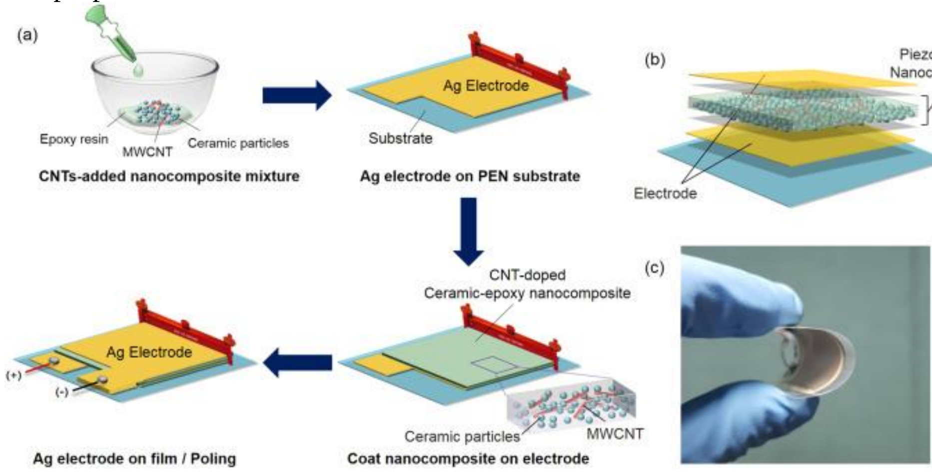

Figure 2. The preparation process of a 0-3 type flexible piezoelectric composite [12].

The other is type 1-3, obtained by arranging piezoelectric ceramic columns in a flexible matrix according to certain rules (Figure 3) [14, 15]. Compared with type 0-3 piezoelectric composites, their dielectric and piezoelectric properties are better, but their mechanical properties are worse [16-18].

In order to retain the piezoelectric properties of piezoelectric ceramics and improve their mechanical properties significantly, porous ceramics can be prepared in advance and then combined with a flexible matrix to obtain 3-3 piezoelectric composites. Compared with 0-3 type and 1-3 type, 3-3 type materials can better combine the advantages of piezoelectric ceramics and flexible matrix and have good dielectric, piezoelectric and mechanical properties. It is an ideal flexible piezoelectric composite material [19].

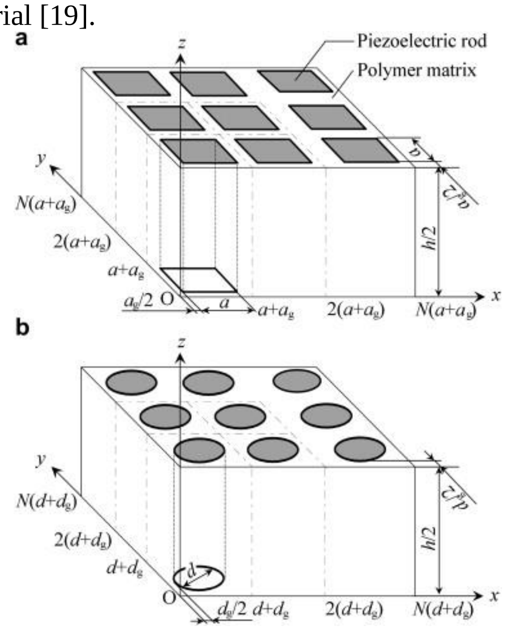

Figure 3. Illustration of 1-3 piezo composite with (a) square and (b) circular rods [14].

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3. Preparation of flexible piezoelectric composites

Compared with other piezoelectric composites, type 3-3 piezoelectric composites have better comprehensive properties and have become a research hotspot of new piezoelectric composites. The ceramic phase of type 3-3 piezoelectric composite has a three-dimensional communication structure with the matrix. Porous ceramics must be prepared first, then composite with the flexible matrix.

There are three common preparation methods for porous ceramics: replica, sacrificial template, and direct foaming (Figure 4) [20].

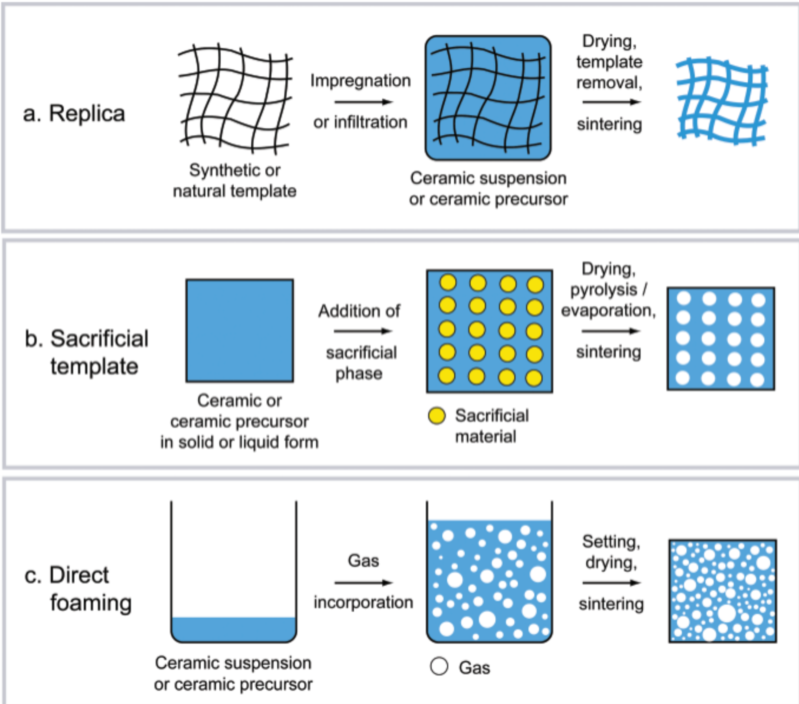

Figure 4. Three ways to produce porous ceramics [20].

The replica method is to impregnate the honeycomb structure with ceramic suspension or precursor solution to produce porous ceramics that exhibit the same morphology as the original porous materials. The sacrificial template method first needs to prepare a two-phase composite material, which includes a continuous matrix of ceramic particles or precursors and a dispersed sacrificial phase. The sacrificial phase is initially evenly distributed throughout the matrix, and after being extracted, pores are generated in the microstructure. The resulting porous material is a reverse copy of the original sacrificial template, opposite to the positive shape obtained by the replica method. The direct foaming method prepares porous materials by passing air into a suspension or liquid medium, then solidifying them to maintain the generated bubble structure. After the consolidation of foam and high-temperature sintering, porous ceramics are obtained. Flexible piezoelectric composites were obtained by impregnating porous ceramics with the flexible matrix.

Wang et al. impregnated sponges in ceramic pastes with different proportions to prepare bulk porous ceramics. They impregnated porous ceramics with a polymer matrix and compounded them with carbon materials to obtain 3-3 PZT/carbon black/epoxy composite piezoelectric ceramics (Figure 5) [19]. This material shows outstanding piezoelectric properties. Its macroscopic appearance is flexible (Figure 6).

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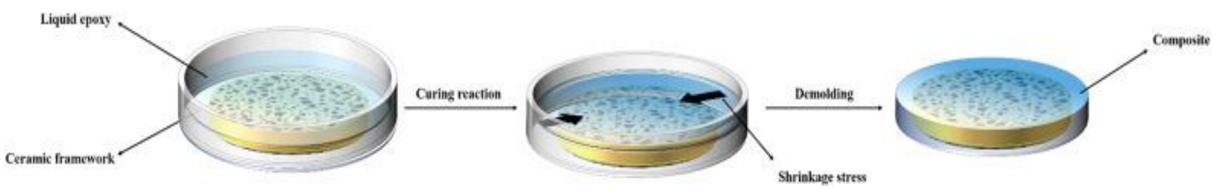

Figure 5. Combination of polymer and ceramic structures [19].

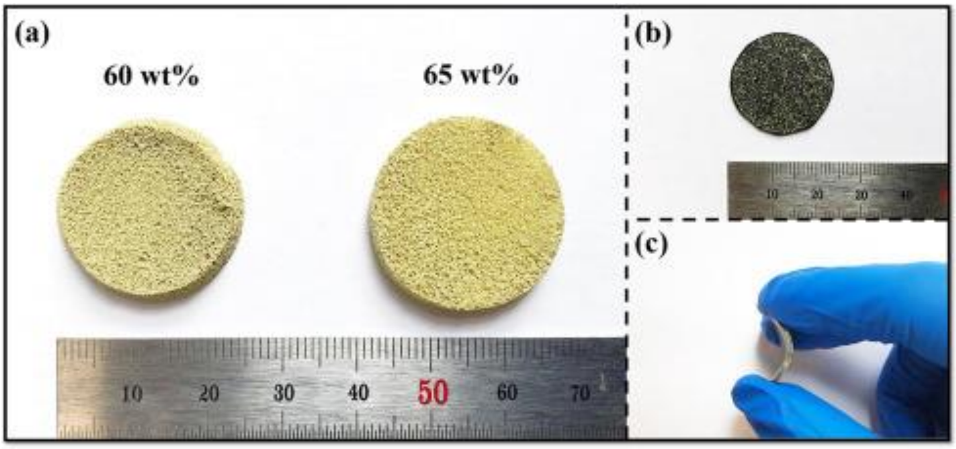

Figure 6. (a) Ceramic morphology with different impregnation rates, (b) macro morphology of complex material, (c) flexibility of complex material [19].

Schipf et al. made 3-3 $BaTiO_3$-epoxy composite disks through adhesive jet printing and epoxy resin penetration after sintering (Figure 7) [21].

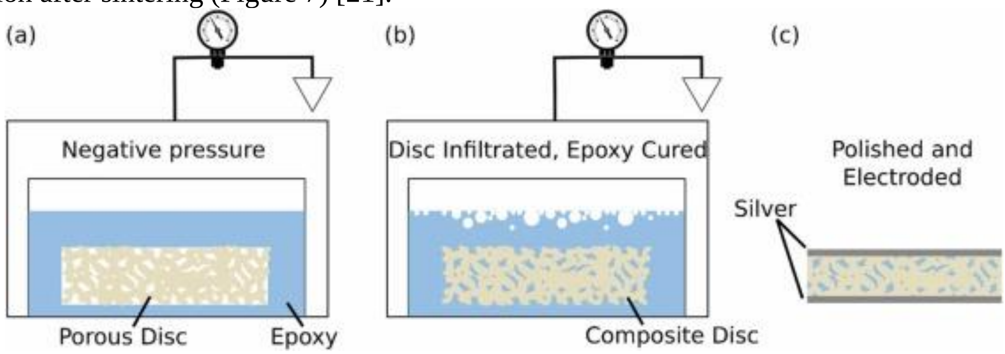

Figure 7. Diagrams showing (a) Composite of a $BaTiO_3$ disk and epoxy, (b) curing of the polymer after immersion, (c) post-treatment of flexible composite disk [21].

They found that increasing the sintering temperature (1350 ℃~1400 ℃) may bring about crystal particle enlargement. The particles of the disk fired at 1400 ℃ are so large that the disk can reflect light from the surrounding environment (Figure 8). The naked eye can observe a white light spot reflected by a grain. The disks fired at a temperature below 1400 ℃ do not have the same degree of visibility.

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Figure 8. A disk fired at 1400 ℃ [21].

4. Characterization of flexible piezoelectric composites

Piezoelectric composites combine the advantages of ceramics with the mechanical flexibility and weight of polymers [22]. The main parameters reflecting the electrical properties of piezoelectric ceramics are piezoelectric constant, dielectric constant, dielectric loss and polarization characteristic curve. Measuring the piezoelectric constant is the most commonly used method to characterize the piezoelectric properties of materials. The piezoelectric constant can directly show the piezoelectric properties of materials.

Li et al. used water as a binder to prepare a PZT paste with a solid matter proportion of 52.0 vol%, showing high storage, loss modulus, and shear thinning characteristics. PZT ceramic scaffolds with different porosity were realized by the direct ink writing method. Then, to obtain flexible piezoelectric composites, the PZT scaffold was compounded with epoxy resin (Figure 9) [23].

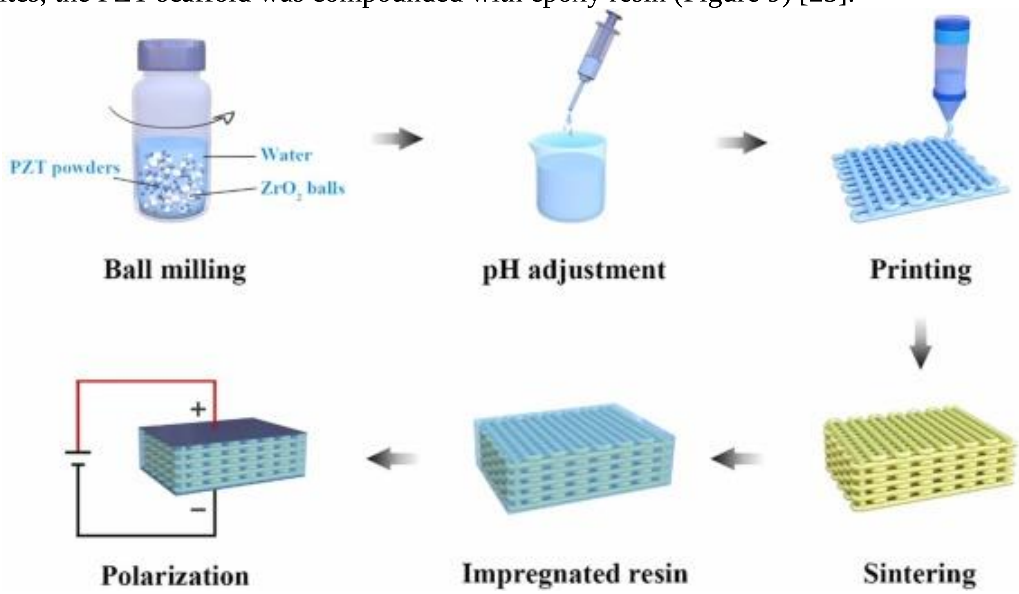

Figure 9. The preparation route of flexible PZT composites [23].

They found that compared with ordinary Z-polarized samples, Y-polarized samples showed higher piezoelectric strain coefficient d_{33} and piezoelectric voltage coefficient g_{33} (Figure 10). For the Y-polarized sample, the maximum value of g_{33} is $81.65\ \mathrm{mV \cdot m/N}$. At this point, the proportion of PZT in it is 34.4 vol% (Figure 11).

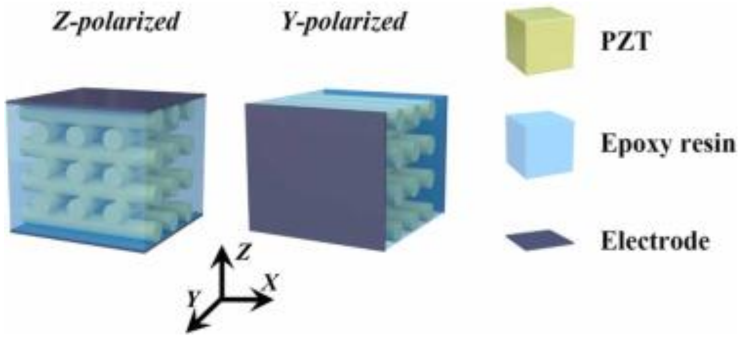

Figure 10. Samples polarized in different directions [23].

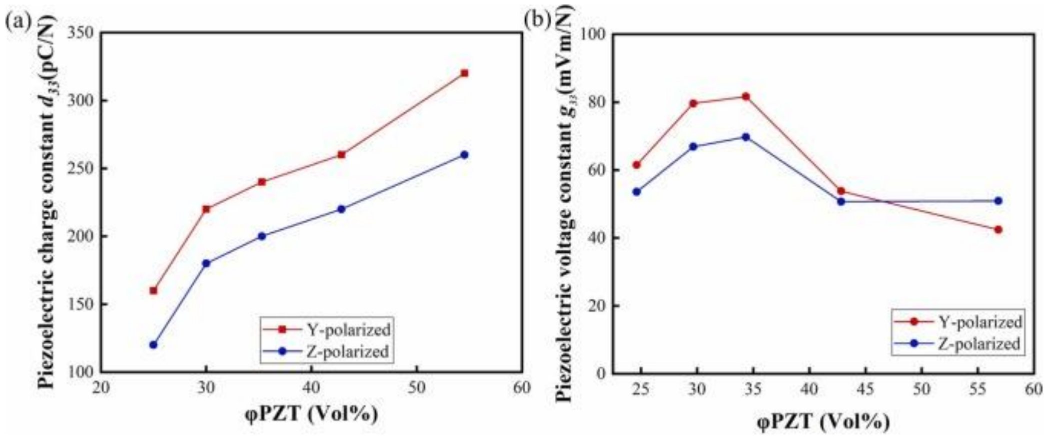

Figure 11. Characterization of electrical properties of two types of samples. (a) d33, (b) g33 [23].

They observed that these two types of flexible materials can show obvious ferroelectricity after polarization in two directions. The residual polarization of Z-polarized samples is $3.29\ \mu C/cm^2$, and for the Y-polarized samples, it can reach a higher measurement result of $5.74\ \mu C/cm^2$. Their difference proves that the Y-polarized flexible materials have more excellent polarization performance (Figure 12).

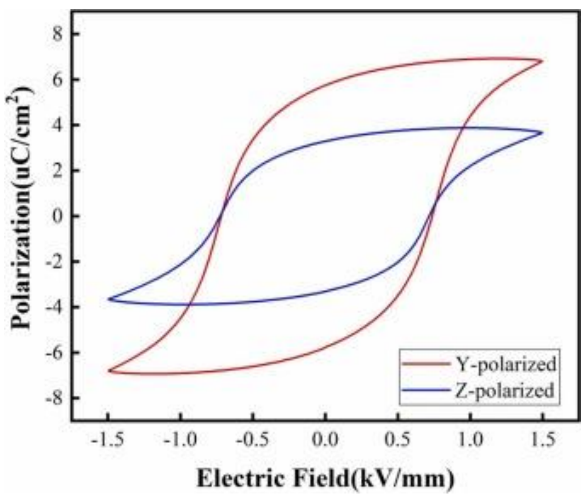

Figure 12. Polarization characteristic curve of two types of samples [23].

5. Conclusions

Piezoelectric ceramics are commonly used ceramic materials with piezoelectric characteristics that can produce deformation under an external electric field and generate bound charges when subjected to external forces. This ability to transform mechanical energy and electrical energy makes it widely used in social production and life, such as ceramic filters, ceramic transformers, ceramic frequency discriminators, high-voltage generators, infrared detectors, surface acoustic wave devices, etc. In order to improve the mechanical properties of piezoelectric ceramics so that they can also be used in flexible devices, wearables and other aspects, relevant research teams have made flexible piezoelectric composites by compounding piezoelectric ceramics with flexible polymer materials. These composites have good elasticity and toughness while retaining piezoelectric properties. Currently, researchers mainly obtain 0-3, 1-3 and 3-3 types of flexible piezoelectric composites, which have advantages and disadvantages in piezoelectric, dielectric, polarization and mechanical properties. At the same time, it should be noted that these composites not only improve the mechanical properties of piezoelectric ceramics but also reduce their piezoelectric properties. It can be predicted that in future research, researchers will make full use of and explore the potential of materials and constantly develop new processes and technologies, aiming to obtain new materials with electrical and mechanical properties superior to the current stage.

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