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# Challenges and progress of chemical modification in piezoelectric composites and their applications

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## Abstract

Piezoelectric materials directly convert energy between electrical and mechanical domains, and have been widely employed in electronic devices as sensors and energy harvesters. Recent research endeavors are mainly devoted to dealing with problems such as high stiffness, brittleness, toxicity, poor durability, and low piezoelectric coefficients. Among developed strategies, chemical modification captures much attention. However, the exact physical properties and direct experimental evidence of chemical modification remain elusive or controversial thus far. In this review, we discuss the recently developed piezoelectric modification strategies for piezoelectric composites and assess the effect of different chemical modification approaches on piezoelectric properties. Moreover, we outline existing challenges and new applications of piezoelectric composites.

**Keywords:** Piezoelectric materials, composite, sensor, energy harvesting, transducer, flexible electronics

## INTRODUCTION

In 1880, French physicists J. Curie and P. Curie found that the surface of quartz crystal generates electric charge under pressure, and the amount of charge is directly proportional to the pressure amplitude, which effect is named the piezoelectric effect[1]. As shown in Figure 1A, the piezoelectric effect is defined as a dual-way electromechanical coupling[2]. When an external force is applied to the material, and we measure the number of charges generated, the unit of the piezoelectric coefficient is C/N; when the material is loaded

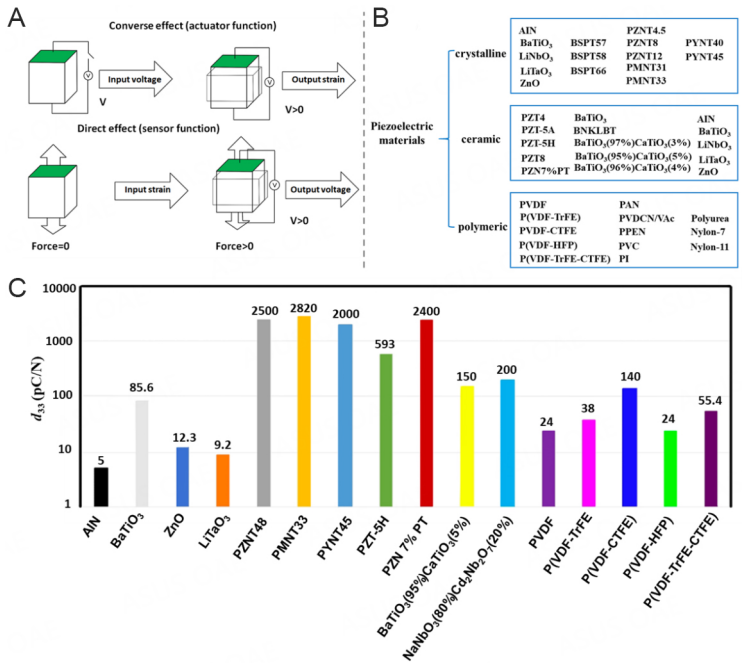


**Figure 1.** The mechanism, classification, and piezoelectric coefficient of typical piezoelectric materials. (A) Converse and direct piezoelectric effects; (B) typical piezoelectric single crystals, ceramics, and polymers; (C) $d_{33}$ of some typical piezoelectric materials. BSPT: $BiScO_3$-$PbTiO_3$; BNKLBT: $(Na,Bi)TiO_3$-$(K,Bi)TiO_3$-$(Li,Bi)TiO_3$-$BaTiO_3$; PZNT: $PbZn_{1/3}Nb_{2/3}O_3$-$PbTiO_3$; PMNT: $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$; PYNT: $PbYb_{1/2}Nb_{1/2}O_3$-$PbTiO_3$; PVDCN/VAc: Poly(ethylene cyanide/vinyl acetate); PPEN: Polyphenyl cyanoether; PZN: $PbZn_{1/3}Nb_{2/3}O_3$; PI: polyimide.

with voltage, and we measure the displacement, the unit of the piezoelectric coefficient is m/V. After more than 100 years of development, scientists have developed different piezoelectric materials, including single crystals, piezoelectric ceramics, and polymers. Figure 1B and C show the different types of piezoelectric materials and compare their longitudinal piezoelectric coefficient ($d_{33}$). According to Damjanovic and Newnham[3,4], the mechanical strain in piezoelectric materials can be induced by an electric field, or external stress governed by Hooke's law, or thermal expansion. Following the Landau Theory[5], we present the classic coupling relationship between the thermal, mechanical, and electrical domains in Figure 2.

Though Piezoelectric ceramics show excellent $d_{33}$, they are rigid and brittle; piezoelectric polymers exhibit sufficient flexibility but usually have a low $d_{33}$. Composite materials combining piezoelectric ceramics into soft polymer matrix have unique advantages, because the composite materials have the flexibility of organic polymer and excellent piezoelectric properties of piezoelectric ceramics. However, (1) how to improve the surface properties of inorganic nano materials; (2) how to improve their dispersion in the polymer matrix; and (3) how to enhance the bonding between ceramics and polymers are three huge challenges. In this regard, researchers proposed high-performance piezoelectric devices by using nanowire growth, transfer techniques, electrospinning, compositing and chemical modification methods[6-8]. Among these approaches, chemical modification has the advantages of simplicity and low cost.

Chemical modification effectively controls the piezoelectric output by tuning the surface charge density of ceramic and polymer materials. For ceramic materials, chemically modified phase structures associated with ionic substitution play an important role in improving piezoelectric properties. Three common lead-free piezoelectric components, namely barium titanate ($BaTiO_3$, BT), potassium-sodium niobate [$(K_{0.5}Na_{0.5})NbO_3$, KNN] and sodium-bismuth titanate [$(Bi_{0.5}Na_{0.5})TiO_3$, BNT] adopt the perovskite $ABO_3$

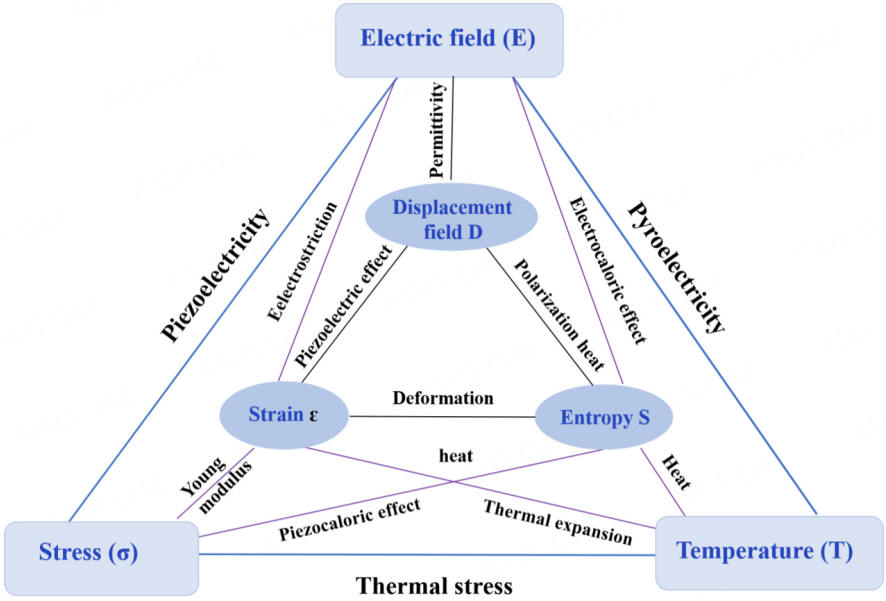


**Figure 2.** The temperature-stress-electric field coupling interaction of piezoelectric materials.

structure, whose chemical substitution usually involves the substitution of cations in the A/B site or both of them [Figure 3A]. For example, for KNN ceramics, the $Li^{+}$[4,9-13] and $Ag^{+}$[14-16] are usually employed to replace A-site ($K^{+}$ or $Na^{+}$), while the $Sb^{5+}$[4,17-19], $Ta^{5+}$[4,20,21], $Zr^{4+}$[1,9,22-24], or $Hf^{4+}$[1,25,26] are commonly used to replace the B-site $Nb^{5+}$ ions to increase the piezoelectric output. The common piezoelectric polymers are PVDF[27-30], poly(tetrafluoroethylene) (PTFE)[31], polyamides/nylons (PA)[32], polyacrylonitrile (PAN)[33,34], and polyoxyethylene (PVC)[35,36], etc. These polymers usually have smaller piezoelectric coefficients than piezoelectric ceramics; thus, except for PVDF and its copolymers, most piezo polymers are not widely adopted in the market. Besides, the strong conformation of the PVDF-based materials can be achieved by direct chemical modification of the polymer, thereby enhancing its piezoelectric properties. The copolymerization reaction is an effective method for preparing $\beta$-PVDF with all-trans planar conformation. Adding comonomers with large spatial hindrance, such as trifluoroethylene (TrFE)[37,38], chloride trifluoride ethylene (CTFE)[39,40], 1,1-chloro-fluoroethylene (CFE)[30,39], hexafluoropropene (HFP)[30,39], will increase the conformational potential energy of $\alpha$-phase copolymer. Figure 3B shows a preparation strategy of P(VDF-TrFE-CTFE) terpolymer, which increases $d_{33}$ to -55.4 PC/N[41]. The simple component elimination method can also get a high $\beta$-phase for PVDF[42-45]. Using a dehydrogenation technology of fluoride [Figure 3C], and the fluorinated alkyne (F.A.) monomers (< 2 mol %) in P(VDF-TrFE-CTFE) terpolymers by dehydrochlorination of CFEs, researchers got an ultrahigh $d_{33}$ of ~1050 pm/V[46]. Although new PVDF-based copolymers present a high piezoelectric effect, their large-scale synthesis remains difficult. Recent efforts have been made to form flexible composite materials consisting of ceramics and polymers to resolve these issues.

Since the classification of two-phase piezoelectric ceramic/polymer composites was first proposed by R. E. Newnham in 1978, more and more attention has been paid to piezoelectric composites on account of their excellent comprehensive properties[3,47,48]. How to improve the dispersion in polymer matrix and enhance the bonding between ceramic and polymer has become an important research direction in ceramic-polymer composites. A uniform dispersion of piezoelectric particles in the composite film is crucial for fabricating piezoelectric materials with high output, as it ensures a uniformly distributed piezoelectric potential within the active energy-harvesting composite layer. Chemical modification creates the opportunity to incorporate

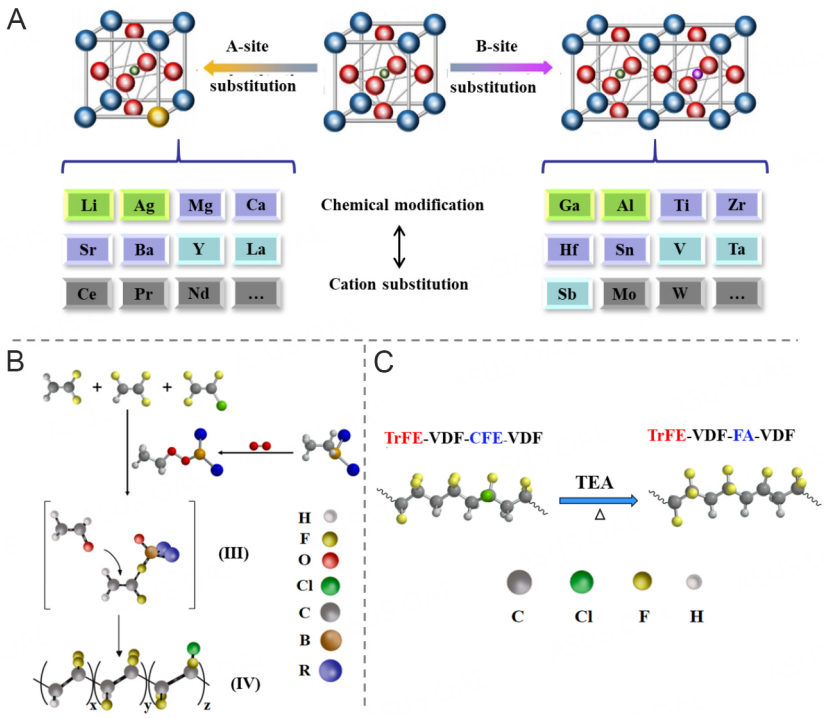


**Figure 3.** Chemically modified piezoelectric materials. (A) Cationic-substitution-modified ceramics; (B) the direct terpolymerization scheme of VDF, TrFE and CTFE[41]. Copyright 2022, American Chemical Society; (C) reaction scheme of P(VDF-TrFE-CFE) treated with triethylamine[46]. Copyright 2022, American Association for the Advancement of Science.

polar molecules into non-polar molecular structures without problems of dispersion and compatibility, thus increasing their piezoelectric properties. In this review, we summarize the recent advances in high-performance piezoelectric composites based on organic surface modification, inorganic functionalization, and organic-inorganic co-modification, focusing on the recent advances in design methods for achieving superior piezoelectric properties. While there have been several excellent reviews on piezoelectric ceramics and polymers[1,49-53], this work highlights the effects of chemical modification on piezoelectric composites. In the meantime, the general design strategies of chemical modification to optimize piezoelectric composites' properties and their application are summarized. Finally, we outline chemical modification's challenges and further development prospects in piezoelectric composites.

## CHEMICAL MODIFICATION IN PIEZOELECTRIC COMPOSITES

Chemically modified composites incorporating piezoceramic particles into polymers have unique advantages such as simple and scalable fabrication, low cost, high mechanical durability, and flexibility. Three non-hazardous chemical treatments, silylation, amidation and grafting, are usually available to modify composites. This section analyzes the research progress into chemically-reinforced piezoelectric composites since 2000. Figure 4 shows the outline of this section.

### Silylation

Silylation reaction usually uses the SiOH group hydrolyzed by trimethoxysilyl or triethylsilane-based elastomers to modify the surface of nano materials, primarily, 3-aminopropyltrimethoxysilane (APS), 3-trimethoxysilylpropyl methacrylate (TMSPM), γ-Glycidoxypropyltrimethoxysilane (KH560) and polydimethylsiloxane (PDMS)[54-59]. In the process of preparing piezoelectric nanocomposites, nanoparticles are easy to agglomerate and show poor affinity with the matrix. Nanoparticles are not miscible when they

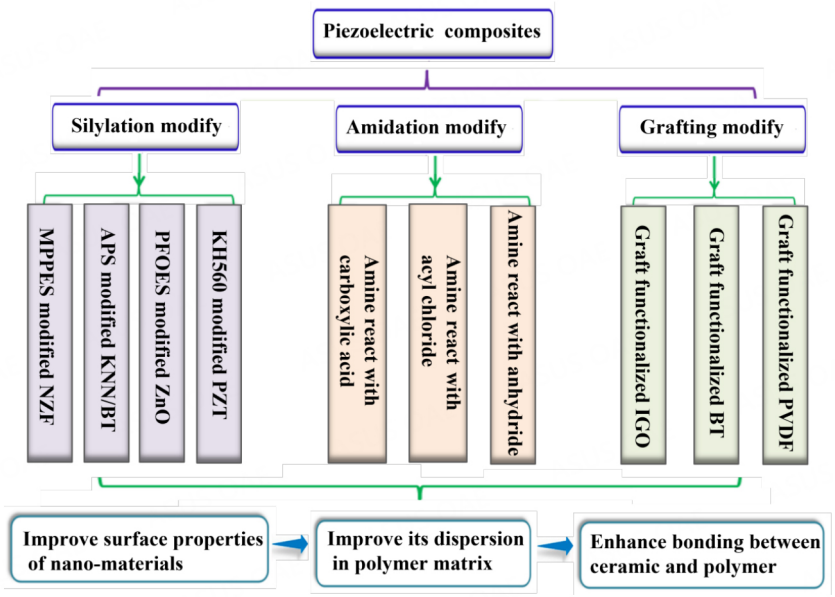


**Figure 4.** Outline of the technical content of chemical modified piezoelectric composites.

are mixed with each other, resulting in voids and phase separation. Chemical modification of nanomaterials can solve this problem well. A silane coupling agent helps nanoparticles scatter and strengthens the interface combination between nanoparticles and polymers. Figure 5A illustrates a typical diagram of silane-modified nanocomposites[60].

APS modifier plays an influential role in maximizing the use of the excellent electroactive phases of PVDF polymer to enhance its piezoelectric response. Bairagi *et al.* found that the growth of PVDF polymer electroactive phases was significantly improved by adding APS-modified KNN nanorods[55]. In particular, the $\beta$ crystal portion of surface-modified KNN nanorod-based films was improved (17% for pure PVDF, 45% for untreated KNN-based films, and more than 50% for surface-modified KNN based films). Figure 5B describes the nucleation mechanism of KNN nanorods in the PVDF polymer matrix[55]. Following that, they added APS-modified KNN nanorods to PVDF electrospinning nets to further enhance the piezoelectric property[56]. The maximum output voltage and current of composite piezoelectric materials are 21 V and 22 mA, respectively, significantly higher than the KNN/PVDF nanogenerator prepared by pure KNN. Also, in another study, Su *et al.* applied APS's properties to modify $BaTiO_3$ nanoparticles[57]. The maximum piezoelectric constant ($d_{33}$) of the direct piezoelectric response for poled $BaTiO_3$-PVDF membranes was approximately 4.8 pC/N, at 0.1 wt% loading of $BaTiO_3$. This result can be attributed to the substitution of -OH groups on the $BaTiO_3$ surface by a silane coupling agent, thus eliminating the formation of adsorbed water on the surface of the particles.

A similar response has been reported with other silane-based coupling agents to modified BTO and PZT nanocomposites. During this process, the silane coupling agent is coated onto nanoparticles to improve the interface interactions and compatibility between the nanoparticles and polymer matrix. Recently, Wang *et al.* demonstrated high-performance $BaTiO_3$-PDMS composites for electromechanical energy conversion[54]. The maximum open-circuit output voltage and short-circuit current of dielectrophoretically aligned $BaTiO_3$-PDMS composite reach ~80 V and ~25 $\mu$A, respectively. Surface modifiers reduce the surface energy of nanofillers to form a repellent tendency between fillers, thus mitigating the agglomeration trend. In 2019, Cui *et al.* prepared piezoelectric metamaterials with complex microstructures by surface

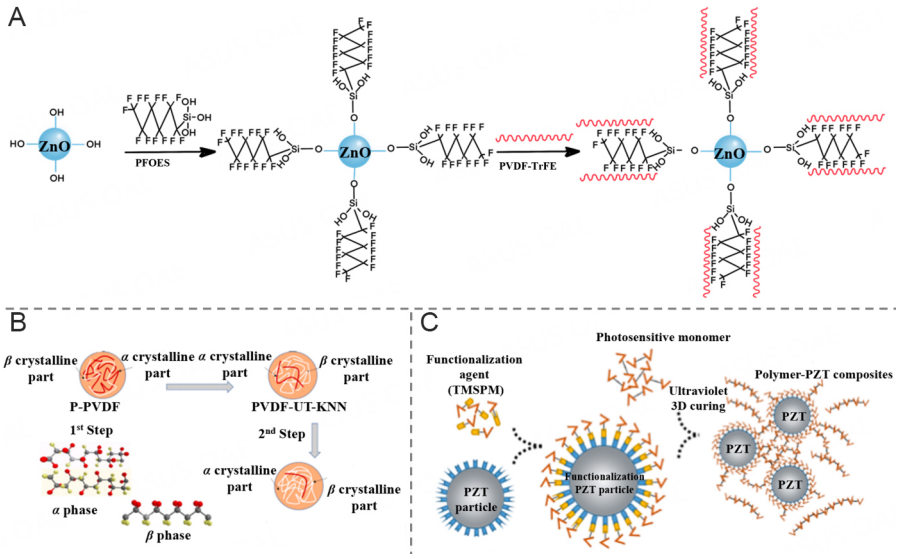


**Figure 5.** Piezoelectric materials chemically modified by silane coupling agents. (A) The schematic diagram of silane coupling agent modified ZnO and PVDF-TrFE[60]. Copyright 2019, Elsevier; (B) *β* nucleating effect of the KNN nanorods in the PVDF matrix[55]. Copyright 2019, Springer US. (C) schematic illustration of surface functionalization method and strong bonds between the nanoparticles and the polymer matrix after the ultraviolet curing process[58]. Copyright 2019, Springer Nature.

functionalization of PZT with TMSPM [Figure 5C][58]. They found that the low-density flexible piezoelectric metamaterial obtained by this method has more than twice the piezoelectric constant than other flexible piezoelectric composites. In addition, Wu *et al.* developed a PZT-type/epoxy piezoelectric composite with a spiral structure by a roll forming-curling method[59]. KH560 first chemically modifies PZT through silylation reaction, and then they graft the KH560 onto the epoxy resin matrix through a condensation reaction, forming a bridge between PZT and epoxy. The study found that after KH560-handling with 12 h, it exhibited the optimal piezoelectric performance with a $d_{33}$ of ~546 pC/N, which is 7.5% above those prepared without the coupling agent.

Piezoelectric composites modified by silane coupling agents show both superior *β*-phase content and charge collecting area. The selection of an appropriate silane modifier is conducive to improving the electroactive phase of PVDF-based polymers and plays a key role in maximizing their piezoelectric properties.

### Amidation

Amidation reaction is described as follows: If ammonia or amine is used to react with carboxylic acid, it is necessary to control the equilibrium conditions to prevent excessive product; If amine and acyl chloride are used for preparation, low temperature and alkali shall be added, and the addition rate of raw materials shall be controlled to control heat release; If amine reacts with anhydride, catalysts such as sulfuric acid and peroxy acid should be added. The mechanism of the amidation reaction is shown in Figure 6A.

Thanks to the strong charge interaction, The covalent bond formed by amidation improves composites' mechanical and electrical properties[61]. In view of this, Mandal *et al.* prepared an ionic liquid (I.L.) integrated multiwalled carbon nanotube (MWNT-IL) by amidation reaction between MWNT-COOH and IL-$NH_2$, as shown in Figure 6B[62]. Their report explained that covalently anchored I.L. could uniformly disperse MWCNT in PVDF matrix, preferentially *β* nucleus due to dipole interaction. Using the same approach, Chen *et al.* synthesized a novel PEG-graphene through an amidation reaction between graphene oxide and methoxypolyethylene glycol amin[63]. The formation of hydrogen bond leads to PVDF

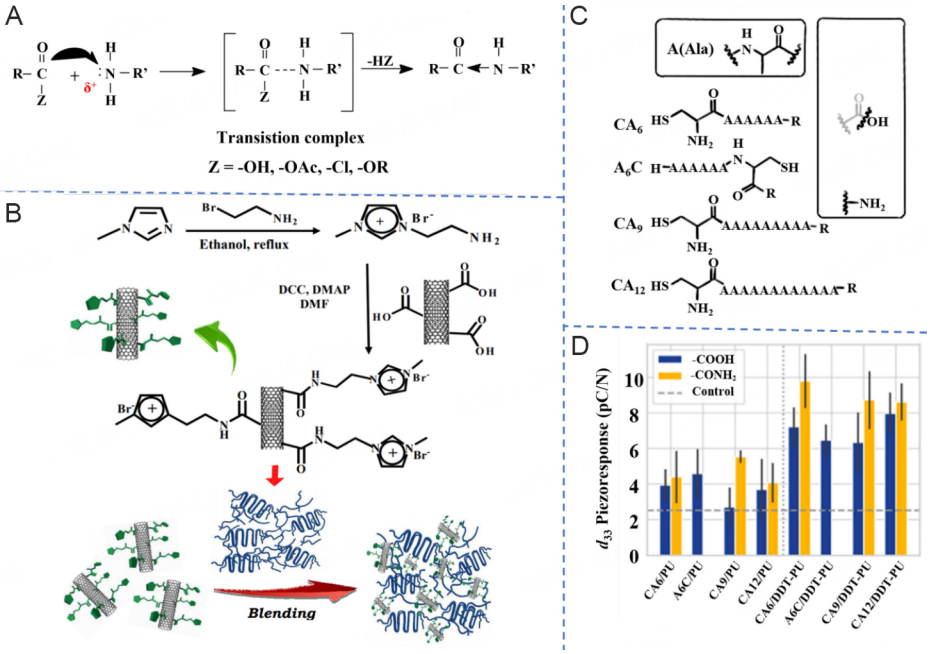


**Figure 6.** Enhancement in the electroactive crystalline phase and dielectric performance of amidated PVDF composites. (A) The mechanism of the amidation reaction; (B) schematic illustration for the dispersion of ionic liquid functionalized MWNTs within the PVDF matrix[62].Copyright 2013, American Chemical Society; (C) chemical structures of peptides used[65].Copyright 2021, Wiley-Blackwell; (D) amide-terminated peptides present higher responses than carboxylate-terminated ones[65].Copyright 2021, Wiley-Blackwell.

macromolecular chain contacting with graphene, forming a $\beta$ phase with perfect TTTT chain sequence. The dielectric constant of 10 wt.% PEG-graphene (53.3) is 6.5 times that of pure PVDF. It is believed that the amidation of nanoparticles and the formation of hydrogen bonds with polymers promote PVDF-based composites with excellent piezoelectric properties.

Furthermore, a few research attempts are applied to improve piezoelectric composites' performance by amidation after modification of nanoparticles and polymers. For example, Pongampai *et al.* propose a triboelectric-piezoelectric hybrid nanogenerator based on $BaTiO_3$-Nanorods/Chitosa[64]. The direct coupling between the BT-NPs and the chitosan matrix makes it trapped in the polymer network, which significantly increases the dispersion of BT-NPs in the chitosan matrix. The harvested open-circuit voltage and current density can get to 111.4 V and 21.6 $\mu$, respectively, sufficient to drive 100 LEDs. Amine functionalization also affects the stability and rigidity of monolayers. Petroff *et al.* manufactured a piezoelectric force and touch sensor with oligopeptides to attain large piezoelectric responses without electro polarization through self-assembly technology [Figure 6C][65]. A maximum value of (9.8 ± 1.5) pC $N^{-1}$ is obtained from the assembly composed of amide-terminated CA6 functionalized printed circuit boards (PCBs) [Figure 6D]. The amidation reduces the $\alpha$-helix, allowing for a dipole change in the deformation under compression, ultimately producing a greater piezoelectric response.

### Grafting

The grafting method uses the chemical reaction between a reactive group on the material surface and the grafted monomer or macromolecular chain. Piezoelectric nanoparticles can be integrated into the composite film through grafting reactions that improve the distribution uniformity of nanoparticles in the polymer matrix. Figure 7A shows the mechanism of the grafting reaction.

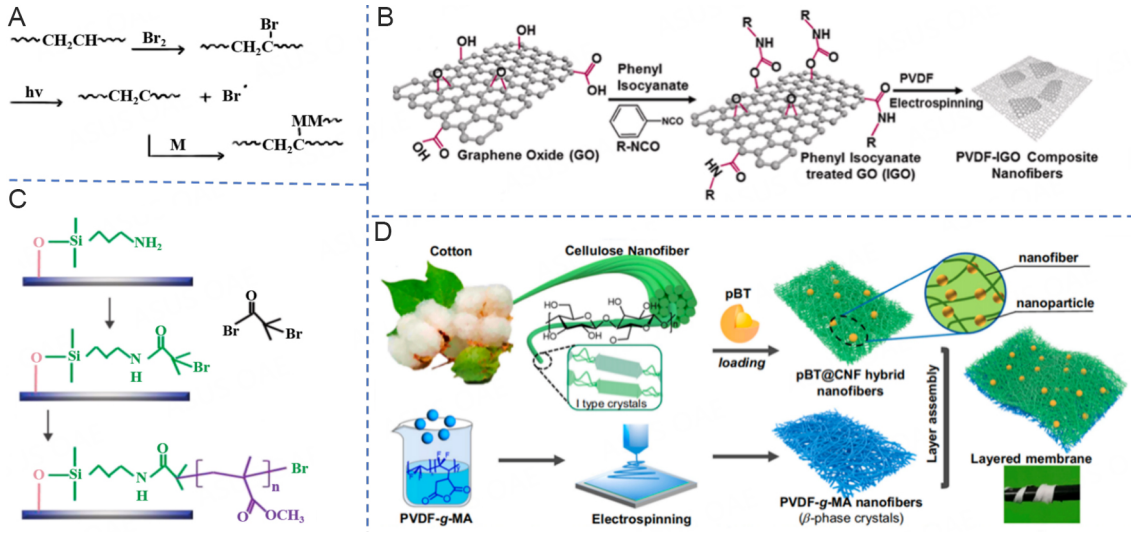


**Figure 7.** Composite piezoelectric films prepared by grafting nanoparticles with polymers. (A) The mechanism of the grafting reaction; (B) schematic of the fabrication of PVDFNF-IGO composite nanofibers[67]. Copyright 2021, Elsevier Ltd; (C) the synthesis procedure of the PMMA@$BaTiO_3$ nanowires by ATRP technology[71]. Copyright 2021, Elsevier BV; (D) schematic illustration of the fabrication of layered CPNF membranes[72]. Copyright 2022, Elsevier Ltd.

Grafting is a simple and economical method to coordinate the interaction of polymers with nanomaterials[64,66]. For instance, Ramasamy *et al.* prepared a PVDF nanofibers sensor by using phenyl-isocyanate graft graphene oxide (IGO), as shown in Figure 7B[67]. The IGO endowed PVDFNFs with a rough surface morphology, enhanced crystallinity, and electroactive $\beta$ phase. Begum *et al.* grafted multiwalled carbon nanotubes (MWCNTs) onto di-glycidyl ether of bisphenol-A (DGEBA) by a linker moiety hexamethylene diamine (HMD)[68]. They reported that the modified MWCNTs (HD-MWCNTs) found firm polar groups on the surface, which improves the compatibility between HD-MWCNTs and PVDF and forms hydrogen bonds. Covalent Functionalization has stronger interaction than the surface modification of non-covalent moieties, allowing PVDF/HD-MWCNTs nanocomposite to achieve $d_{33}$ up to 5.0 pC/N at a filler loading of 1 wt%[69,70].

A different work focuses on grafting polymethyl methacrylate (PMMA) onto $BaTiO_3$ nanowires through atom transfer radical polymerization (ATRP) technology [Figure 7C][71]. The polymer grown from the inorganic filler surface in situ ATRP produces a strong interface with the fillers, and endows nanocomposites with increased dielectric constant and ultra-low dielectric loss[71]. As expected, PMMA grafting of $BaTiO_3$ nanowires resulted in a more uniform dispersion in the PVDF-TrFE matrix and an improved stress transfer at the interface between them. They report a maximum export voltage of 12.6 V and output power of 4.25 $\mu$W in composites at 10 wt% filler concentration; it is 2.2 times and 7.6 times upper than that of the composites with unmodified $BaTiO_3$ and without $BaTiO_3$ nanowires.

Interestingly, grafting reaction can take place on polymers surface. Wang *et al.* developed a layered piezoelectric nanogenerator using maleic anhydride grafted PVDF covalently bonded to cotton cellulose nanofibers (CNF) [Figure 7D][72]. These membranes show a clear double-layer structure, and the PBT@CNF layer in all membranes is tightly attached to the PNF layer, and there is no observation of layers and gaps. Under strong interface interaction, the maximum tensile strength of double-layer CPNF film is 47.99 ± 4.08 MPa at 5.0 wt% pBT. The layered PENGs produce significantly reinforced piezoelectricity, increasing $d_{33}$ from 1.63 to 27.2 pC/N as the loading of pBT from 0% to 5.0 wt%[73,74]. A maximum in the output

**Table 1. A survey of the main parameters of piezoelectric composites**

| Material system | Modification | $d_{33}$ (pC/N) | Frequency | Dimensions | Voltage (V) | Ref. |
|---|---|---|---|---|---|---|
| PVDF/ZnO N.W.s | - | - | 1 Hz | - | 0.2 | [75] |
| PVDF/$BaTiO_3$ | - | - | 1 Hz | 1.5 * 2 $cm^2$ | 6.7 | [76] |
| PVDF/KNN NRs | - | - | 10 Hz | 2 * 2 $cm^2$ | 3.4 | [77] |
| P(VDF-TrFE)/KNN | - | - | 5 KHz | - | 0.98 | [78] |
| P(VDF-TrFE)/AgNPs | - | - | - | 35 * 35 $nm^2$ | 0.048 | [79] |
| P(VDF-TrFE)/ZnO | - | 19.0 | 190 Hz | 13 * 13 $mm^2$ | - | [80] |
| PVDF/graphene | PFOES | 39.8 | 1 Hz | - | - | [81] |
| P(VDF-TrFE)/$BaTiO_3$ | PA | - | 3 Hz | 2.5 * 2.5 $cm^2$ | 6.0 | [82] |
| P(VDF-TrFE)/$BaTiO_3$ | PMMA | - | 3 Hz | 2.5 * 2.5 $cm^2$ | 12.6 | [71] |
| PVDF/KNN | APS | - | - | - | 21.0 | [56] |
| SEBSm/PZT | PEI | - | - | 2 * 4 $cm^2$ | 65.0 | [83] |

performance ($V_{oc}$ = 3.2 V, $I_{sc}$ = 0.25 $\mu$A) is achieved at a 5.0 wt% pBT loading. The significant improvement in piezoelectric output is attributed to the synergistic effect of these piezoelectric elements in the layered structure and the local stress concentration caused by the rigid pBT nanoparticles.

Table 1 shows the preparation and some parameters of new piezoelectric composites[56,71,75-83]. Compared with similar polymer matrix composites injected with carbon nanotube fillers or unmodified nanoparticles, the piezoelectric coefficient of chemically modified composites is significantly improved. In summary, chemical modification is a straightforward technique for enhancing the performance of piezoelectric composites.

## APPLICATION

Piezoelectric composites offer mechanical flexibility, suitable voltages with sufficient power output, lower manufacturing costs, and ease of rapid processing compared to ceramic and polymer materials. They thus have a great potential to benefit a diverse set of applications. This section explores the application of chemically modified piezoelectric composites in sensors, energy harvesters, and acoustic transducers.

### Sensors

Sensors based on piezoelectric composites can respond to changes in physical quantities, such as pressure, sound waves, and airflow. Its sensitive element is made of piezoelectric materials, and when the piezoelectric material is subjected to an external force, charges will be formed on its surface. After the charge passes through a charge amplifier, the amplification of the measurement circuit, and the impedance transformation, it will be converted into an electrical output proportional to the external force received.

Pressure sensors are used in sporting gloves for simultaneous impact absorption and punching force mapping. Hong *et al.* developed a 3D-printed flexible piezoelectric nanocomposite with a tensile dominant micro-mechanical structure with a design thickness (5 mm)[84]. Then, boxing gloves were inserted to provide spatial and temporal resolution mapping of the reaction force applied to the hand joints during boxing activities[84]. They first functionalized the nanoparticles and covalently grafted them onto the surface of the piezoelectric nanoparticles. Then, they combined the modified piezoelectric particles with the photopolymer after curing by covalent chemical bonds ($CH_2$-$CH_2$ groups) under UV light [Figure 8A]. The 3D-printable piezoelectric nanocomposites designed by chemical modification exceed the existing compliance and functional performance trade-offs, highlighting their potential as flexible sensors and wearable devices. Compared to the commercial PVDF ($d_{33} \approx 27$ pC $N^{-1}$), functionalized piezoelectric

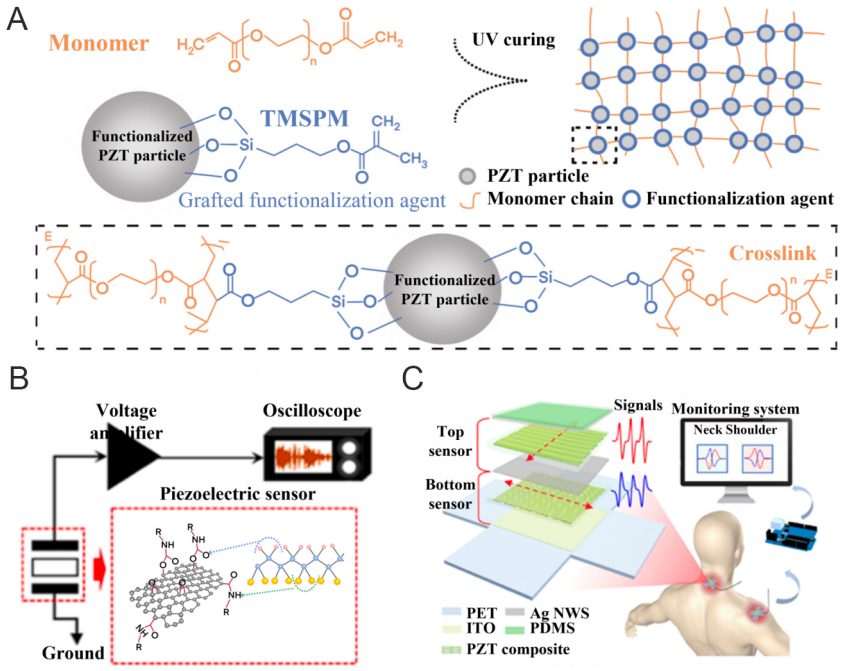


**Figure 8.** Piezoelectric composites in sensors. (A) Chemical structure of the UV-sensitive monomer matrix and the functionalized PZT particles[84]. Copyright 2019, Wiley-VCH Verlag; (B) the experimental setup used to measure the output voltages/sensitivities of the piezoelectric sensors[67]. Copyright 2021, Elsevier Ltd; (C) the kirigami-structured HAPNC sensor to monitor MSDs[85]. Copyright 2021, American Association for the Advancement of Science.

composite has a higher piezoelectric charge constant $d_{33}$ (≈ 110 pC $N^{-1}$). Ramasamy *et al.* grafted phenyl isocyanate on the surface of graphene oxide, and blended it with PVDF by electrospinning to prepare a composite piezoelectric material [Figure 8B][67]. The functionalization of phenyl isocyanate on the surface of graphene oxide can enhance its dispersion in organic solvents, conducive to its effective hybridization with PVDF. At 10 MΩ load resistance, the PVDFNF-IGO composite displayed the optimal piezoelectric property with an output voltage of 22.8 V and a power of 51.984 μW, 24.6% higher and 55.23% upper than those of the original PVDFNFs, respectively. Furthermore, the sensor sensitivity of the composites is 63.09% higher than that of the pristine PVDF.

In addition, sensors are also well used in artificial intelligence. In our lab, a 3D-interconnected piezoelectric composite was manufactured to monitor the motions of a soft robot[85]. The piezoelectric composite is the core sensory element. A lead zirconate titanate (PZT) ceramic network is constructed in Kirigami honeycomb grids and then filled with polydimethylsiloxane (PDMS) [Figure 8C]. Through silane modification, the designed kirigami structure has a high piezoelectric sensitivity (15.4 mV $kPa^{-1}$) and high linearity ($R^2$ = 0.98) compared to the composite with randomly dispersed fillers. Piezoelectric sensors show many advantages, including extensive measurement range, high voltage electrical anisotropy, and long-term monitoring capability.

### Energy harvesters

The basic working principle of the piezoelectric energy harvester is the piezoelectric effect, that is, the deformation of the piezoelectric material under the excitation of the external vibration causes the asymmetry of the dipole inside the material and the polarization phenomenon. At the same time, electrical charges are accumulated on surface electrodes. Detailed information on energy harvesters can be found in the review papers[86,87]. Our group analyzed the dynamic responses of energy harvesters excited by vibrations

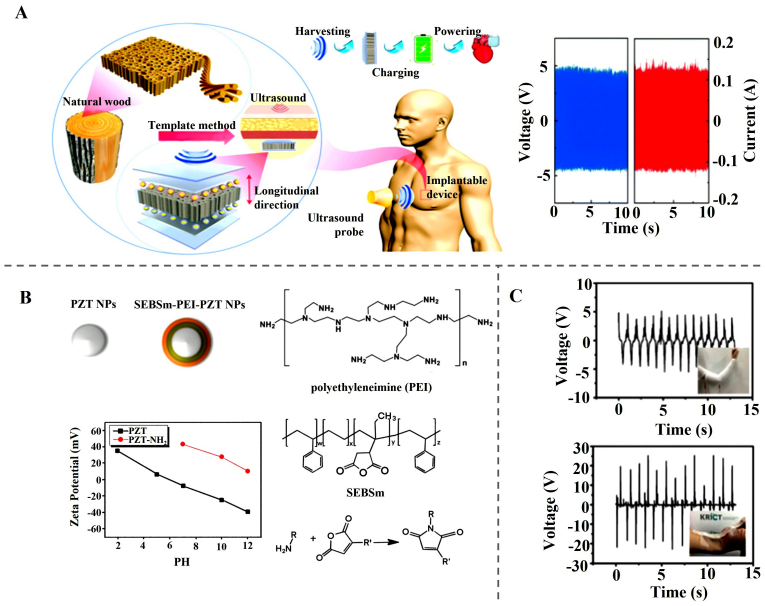


**Figure 9.** Piezoelectric composites in energy harvesters. (A) Schematic illustration showing the structure of the W-PUEH device based on natural wood with lattice-like cellulose channels[89].Copyright 2021, Royal Society of Chemistry; (B) the PZT NPs are surface-functionalized with amine groups.[83] Copyright 2018, Royal Society of Chemistry; (C) the generated output voltage (open-circuit voltage) from the PNG device attached to the elbow and wrist when subjected to bending[83].Copyright 2018, Royal Society of Chemistry.

from multiple directions using a nonlinear compressive-mode PZT plate[88], which enhanced the practicability of energy collection in complex environments. Moreover, we developed a transmuscular ultrasonic wireless energy transfer system based on a flexible wood-templated piezoelectric energy harvester [Figure 9A]. It can output open circuit voltage (~4.5 V) and short circuit current (~120 μA), all meeting biomedical equipment's needs[89].

Recently, several research attempts have been carried out to improve the performance of energy harvesters by amidation after modification of nanoparticles and polymers, respectively. For instance, Yao *et al.* developed a PZT flexible piezoelectric energy harvester by amidation of PZT and triblock copolymer[83]. This chemically reinforced composite contains stably dispersed PZT nanoparticles in the polymer matrix. It performs excellently under bending strain, with a high output voltage of 65 V and a current of 1.6 $\mu$A [Figure 9B]. It can also collect the energy generated during the movement of upper arm muscles, as shown in Figure 9C. The above work shows that the output voltage of piezoelectric energy harvesters usually reaches tens of volts, enough to drive most electronic devices in daily life.

### Acoustic transducers

Piezoelectric transducers operate in the acoustic spectrum range, including audio, ultrasonic, and infrasonic frequency ranges[90]. They use the piezoelectric effect and resonance to convert electrical energy into mechanical vibration. Many composite-based ultrasonic transducers have been reported[91-95], and we here choose two studies to illustrate the performance differences between different composites.

Electrical stimulation produced by piezoelectric materials can enhance nerve regeneration to treat neurodegenerative diseases. Jiang *et al.* proposed a piezoelectric patch (LF-PUEH) based on flexible

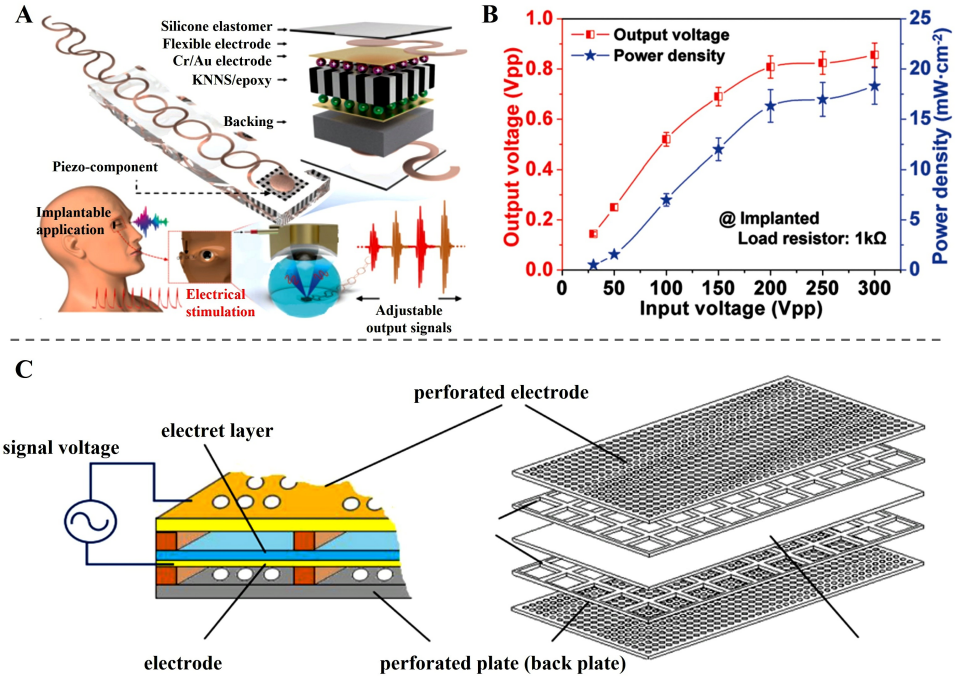


**Figure 10.** Illustration of piezoelectric composites in the acoustic transducers. (A) Schematic and design of the flexible LF-PUEH device[95]. Copyright 2019, Wiley-VCH Verlag; (B) output voltage and power density of the device as a function of input voltage[95]. Copyright 2019, Wiley-VCH Verlag; (C) schematic of a flexible electret loudspeaker, and an exploded view of a flexible electret loudspeaker[96]. Copyright 2010, IOP Publishing Ltd.

high-performance KNNS/epoxy 1-3 arrays[95]. As shown in Figure 10A, LF-PUEH is implanted into the eyeball. Wirelessly excited by a transducer that operates at 100 $V_{pp}$, the LF-PUEH shows a voltage response of 0.54 $V_{pp}$ and a power density of 7.3 mW·cm$^{-2}$ [Figure 10B], above the power threshold required for stimulating the retinal nerve. In addition, piezo transducers are also used as loudspeakers [Figure 10C][96]. A loudspeaker is unique in that its sound pressure level is a quality factor; that is, the effective sound pressure is the pressure relative to the reference environment[90]. In order to meet the increasing demands, innovative piezoelectric transducers with advanced materials and structures are emerging.

For piezoelectric transducer applications, some devices cannot be replaced by lead-free piezoelectric composites in a short period of time due to some thorny issues such as low strain response and poor temperature stability. Researchers should pay more attention to these thorny issues by chemically modifying lead-free piezoelectric composites to fabricate simple, robust and large-scale piezoelectric transducers for commercial mass production in the future.

## CONCLUSIONS AND OUTLOOK

This review sorts out the design and preparation progress of chemically-reinforced high-performance piezoelectric composites in recent years, and preliminary evaluates the feasibility of the implementation of this scheme. The chemical methods promote the design of piezoelectric composites and help the application of piezoelectric functional systems in energy, medicine, and environmental engineering. In the future research process, further development of piezoelectric composites needs to consider the following aspects.

1. Modifier selection: Metal-organic frameworks are a new type of porous crystal hybrid materials, which allows the insertion of charges and molecules, and can effectively induce strong interfacial coupling effects in polymers. It is expected to be an excellent modifier for piezoelectric composites.

2. Chemical modification selection: The piezoelectric properties of the material are largely affected by the preparation process and the proportion of raw materials. Different chemical modification methods or a combination of multiple modification methods should be selected according to the material properties.

3. Combined with theoretical simulation: Computational simulation would facilitate our understanding of the surface chemical states of materials, and provide new ideas and theoretical guidance for the chemical modification technology of piezoelectric materials.

Overall, since the research on chemically modified piezoelectric composites is still at an early stage, great attention should be paid to modifier selection, compatibility, flexibility, and long-term stability. It is believed that in the near future, chemically modified lead-free piezoelectric composites will play a greater role in the overall piezoelectric materials and their applications.

## DECLARATIONS

### Authors' contributions

Investigation and writing-original draft: Zhang W
Writing-review and editing: Zhang Y, Yan X, Hong Y, Yang Z
Supervision: Yang Z

### Availability of data and materials

Not applicable.

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### Conflicts of interest

All authors declared that there are no conflicts of interest.

### Ethical approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.



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