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Study on relaxor polymer interface matrix for piezoelectric nanocomposite generators

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ABSTRACT

Piezoelectric nanocomposites consisting of a polymer matrix and ceramic fillers are candidate components of flexible, wearable, and self-powered electronic devices. The physical discrepancy between ferroelectric polymers and ceramics in a piezoelectric interface makes it difficult to assemble efficient hybrid piezoelectric nanocomposites without polarization and extraneous artifacts. Here, we describe the effect of a relaxor ferroelectric terpolymer matrix on the piezoelectric output, which can enhance the energy harvesting or sensor performance of piezoelectric composite device of nanocomposite generators with filler nanoparticles of lead zirconium titanate. The dielectric property and reduced ferroelectric hindrance of the proposed terpolymer matrix provides more poling to align the polarization of piezoelectric ceramic fillers compared with a normal ferroelectric copolymer matrix. Therefore, relaxor ferroelectric polymers can be better than normal ferroelectric polymers as the matrix of hybrid polymer-ceramic piezoelectric nanocomposite. This research provides important physical information about the interface between a polymer matrix and ceramic fillers in flexible piezoelectric nanocomposite applications.

1. Introduction

Piezoelectric materials that convert mechanical strain into electrical potential are based on non-centrosymmetric crystals, which lack inversion symmetry. For effective piezoelectric devices, it is important to align the polarization of the ferroelectric domain by applying an external electric field through a process known as poling. After removing the applied electric field, the configuration of the aligned polarization in the ferroelectric domain is fixed, and it can exhibit comprehensive and macroscopic piezoelectric behavior [1]. Most piezoelectric materials are perovskite oxides (*e.g.*, Pb $(Zr,Ti)O_3$ or, PZT), but ferroelectric polymers such as polyvinylidene difluoride (PVDF)-based polymers are also well known as flexible piezoelectric materials [2–4].

Ferroelectric polymers based on PVDF have attracted research attention because of their non-toxic nature, mechanical flexibility, ease of processing and cost-effectiveness. PVDF-based polymers exist in α, β, γ, and δ phases, depending on the chain conformation and tacticity [4–6]. The non-polar α phase is the most thermodynamically stable and does not exhibit piezoelectric properties, whereas the β, γ and δ phases are polar [4,7,8]. The strongest ferroelectric properties are shown by the β phase in which the dipole moment can be aligned in parallel. It is therefore important to increase the β phase content in PVDF-based polymers to enhance the piezoelectric effect, which can be induced by thermal annealing, mechanical drawing, and other methods. [8–10]. Poly (vinylidene fluoride-*co*-trifluoroethylene), P(VDF-TrFE) copolymers have a particularly high β phase content among PVDF-based

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polymers, resulting in strong ferroelectric and piezoelectric characteristics [11–13]. Nevertheless, the piezoelectric properties of P(VDF-TrFE) are relatively low when applied to device performance, compared with ferroelectric perovskite oxides such as PZT [14–19]. Hybrid piezoelectric composites using both a ferroelectric polymer matrix and ferroelectric ceramic micro- or nanoparticle fillers offer the advantages regarding both mechanical flexibility and high piezoelectric output [17,20–23].

However, the assembly of hybrid piezoelectric composites is complicated by several factors. Piezoelectric ceramics have positive longitudinal piezoelectric coefficients (d_{33}), whereas those of a PVDF-based polymer are negative [7,24,25]. The signs of piezoelectric coefficient in other modes are also opposite. This discrepancy causes ineffective or offset polarization between the ferroelectric polymer matrix and the ferroelectric ceramic fillers during poling, a problem that has been ignored or rarely studied. Although multiple poling processes can be used to generate unidirectional polarization, they have yet to be proven effective, and reproducibility is poor [26–30]. For this reason, elastomeric polydimethylsiloxane (PDMS) is often used as a non-piezoelectric matrix in piezoelectric composite devices [31,32], but such devices suffer from poor dielectric properties, triboelectric artifacts, strain dissipation caused by low elastic moduli, and interfacial separation. It is therefore essential to physically examine electroactive polymers suitable for the matrixes of hybrid piezoelectric composites.

Relaxor ferroelectric polymers have robust dielectric properties and high saturation polarization, but there is almost no piezoelectric effect, as is the case for many relaxor ceramics [33–35]. Representative relaxor polymers are PVDF-based terpolymers such as poly (vinylidene fluoride-trifluoroethyleme-chlorofluoroethylene), P(VDF-TrFE-CFE) and, poly (vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene), P(VDF-TrFE-CTFE). These relaxor terpolymers exhibit slim polarization-electric field (*P-E*) hysteresis compared with normal ferroelectric polymers [4,34,36,37]. Relaxor polymers have a small amount of energy loss and remnant polarization, but adequate dielectric properties. Relaxor polymers can effectively respond to an external electric field, but without ferroelectric and piezoelectric hindrance.

Herein, we investigate piezoelectric composites using either a normal ferroelectric P(VDF-TrFE) copolymer or a relaxor P(VDF-TrFE-CTFE) terpolymer as a matrix with piezoelectric PZT filler nanoparticles to evaluate the effect of piezoelectric polymer matrixes on the effectiveness of poling and piezoelectric composite devices. A comparison of the energy-harvesting abilities of two PVDF-based polymer matrixes revealed that the augmentation effect of poling on the piezoelectric output of nanocomposites when using the relaxor polymer as the matrix was higher than when using the ferroelectric polymer as the matrix. This is due to the negative longitudinal piezoelectric coefficient of the P(VDF-TrFE), which cancels the main poling effect of PZT filler particles, which have a positive longitudinal piezoelectric coefficient. The 'polarization collision' between a ferroelectric polymer matrix and a ferroelectric ceramic filler is insufficient to fabricate flexible nanocomposite energy harvesters. This research provides essential information to support the selection and development of a dielectric matrix in composite-based piezoelectric devices for wearable sensor and energy applications.

2. Experimental section

2.1. Materials and fabrication of nanocomposite piezoelectric generators

P(VDF-TrFE) 65/35 mol% and P(VDF-TrFE-CTFE) 65/31/4 mol% were purchased from PolyK Technologies, USA. PZT particles was purchased from APC International, Ltd. Solutions of P(VDF-TrFE) and P (VDF-TrFE-CTFE) were prepared using an *N*, *N*-dimethylmethanamide (DMF) solvent at a concentration of 14 wt%. The PVDF-based polymer powders were dissolved into the DMF with the magnetic stirring bars at room temperature for 24 h. The magnetic stirring bars were continuously rotated in a beaker to dissolve them at 300–600 RPM according to certain viscosity. Piezoelectric composites were created by mixing 5 wt% of ball milled PZT nanoparticles into polymer solutions. The composite mixture was poured onto a 2 × 2 cm^2 indium tin oxide /polyethylene terephthalate (ITO/PET) (Sigma-Aldrich), which served as a bottom electrode substrate and spin casted to create a composite film with the thickness of 15–20 μm as shown in the SEM image (Fig. S1a). The fabricated nanocomposite was dried at 70 °C for 16 h in vacuum oven and annealed at 130 °C for 12 h to stabilize their phases [38]. After the annealing process, the conductive Ni tape was mounted onto the polymer or composite layer as the top electrode, and poling was conducted for 12 h at the Curie temperatures of each polymer matrix with input voltage of 1 kV. Fabrication of pure polymer-based generators used the same procedures except for the mixing of PZT nanoparticles. The fabricated device is flexible and retains its shape well even in bending motion (Fig. S1b). The total fabrication process is illustrated in Fig. S2.

2.2. Measurement and characterization of nanocomposite piezoelectric generators

Field-emission scanning electron microscopy (FE-SEM) (SUPRA40VP, Zeiss) was used to provide microscale images of nanoparticles and nanocomposites. Attenuated total reflection infrared (IR) spectroscopy (Frontier, Perkin Elmer) was used to confirm the phase status and C—F bonding characteristics of both fluoropolymers. X-ray diffraction (XRD) (X'PERT-PRO, PANalytical) patterns as used to characterize the crystals of polymers and ceramics. All instruments were used in the Center for University-wide Research Facilities (CURF) at Jeonbuk National University. The longitudinal piezoelectric coefficient (d_{33}) values were measured by a d_{33} meter (YE2730A, SINOCERA). To confirm the deviation of d_{33} values, the average of more than five different measured data points and more than three samples were used. The dielectric constant and loss in frequencies from 1 kHz to 1 MHz were measured with an inductance, capacitance, and resistance (LCR) meter (4284A, Hewlett Packard). Ferroelectric and dielectric breakdown characteristics were evaluated by a ferroelectric analyzer (PolyK Technologies) at 1 Hz and room temperature. Measurements of the temperature-dependent dielectric constant were analyzed with an impedance analyzer (E4990A, Keysight) between 7 and 170 kHz. The voltage and current signals of the piezoelectric nanocomposite generators were measured with an electrometer (6514, Keithley).

3. Results and discussion

P(VDF-TrFE) copolymers are widely used in actuators, sensors, and energy harvesting devices because of their ferroelectric properties, remnant polarization, and ability to convert mechanical strain into electrical potential [7,38,39]. A detailed chemical formula and the chain structure of P(VDF-TrFE) appear in the top panel of Fig. 1a. P(VDF-TrFE) has clear domain regions with ferroelectric polarization, as shown on the left side of Fig. 1a. Before external electrical poling, dipoles form in the same direction within a certain ferroelectric domain, but the directions of the polarization of the domains are distributed randomly. When an external electric field is applied, in poling, the polarizations align in similar directions. Even after removing the external field, most of the aligned domain directions remain in P(VDF-TrFE) as ferroelectric characteristics. Because P(VDF-TrFE) copolymers have negative longitudinal piezoelectric coefficients in terms of the alignment of strain and polarization [7], the piezoelectric response of PVDF-based ferroelectric polymers are opposite to those of general piezoelectric ceramics. However, this phenomenon has often been ignored and few attempts have been made to understand the electroactive nature of the polymer when fabricating hybrid ferroelectric composites and devices. In contrast with normal ferroelectric polymers, relaxor ferroelectric polymers have stable dielectric constants, high specific capacitance and low remnant

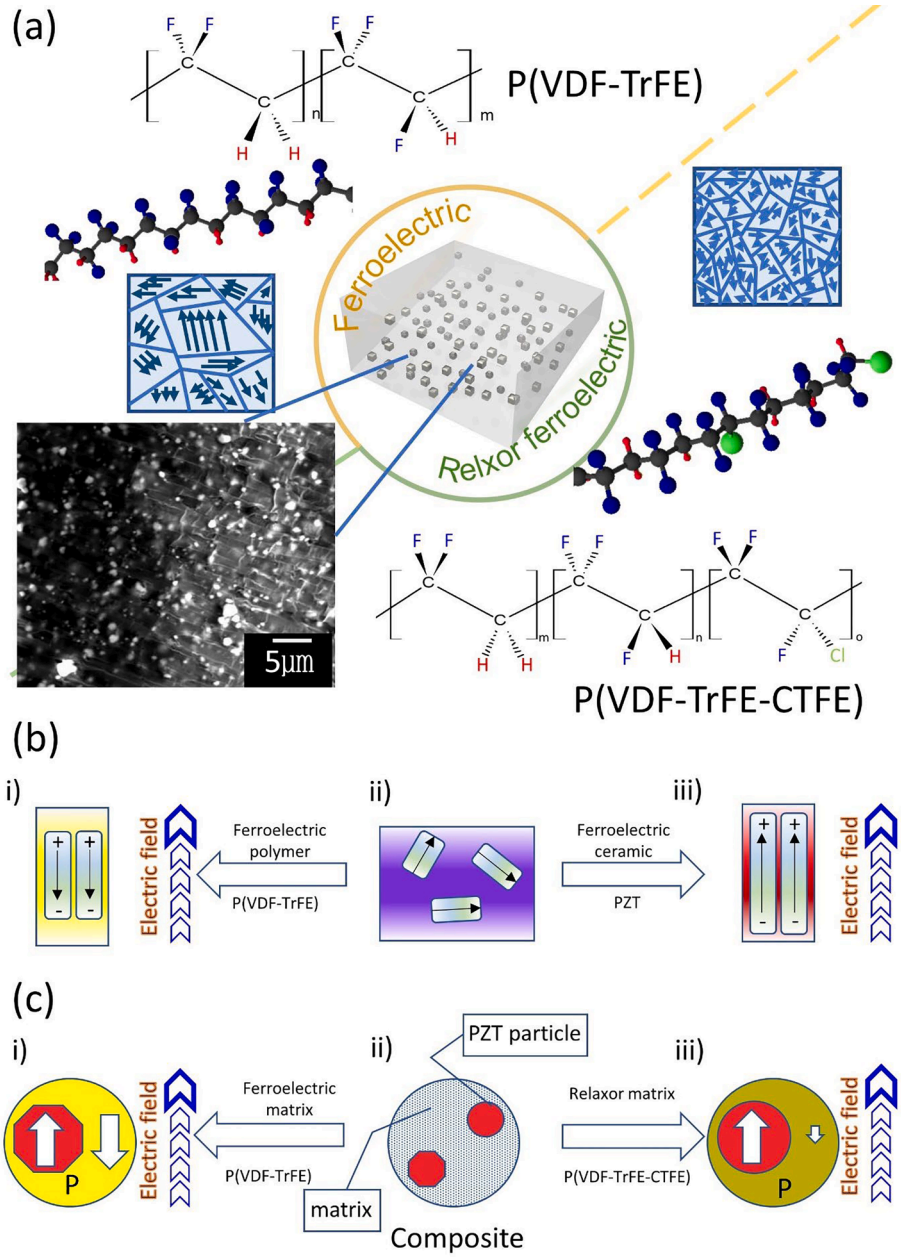

Fig. 1. (a) Conceptual illustrations of two different piezoelectric composites using either the normal ferroelectric polymer (P(VDF-TrFE)) or the relaxor ferroelectric polymer (P(VDF-TrFE-CTFE)) with piezoelectric PZT nanoparticle fillers. The ball and stick models as well as the chain conformation diagram show each polymer structure (black: C, blue: F, red: H, green: Cl). The normal ferroelectric P(VDF-TrFE) presents ferroelectric domain structure whereas the relaxor has polar nanoregion structure. The inset show the cross-sectional SEM of piezoelectric composites consisting of ceramic particles-embedded polymers. (b) Schematics indicating each case of piezoelectric responses of ferroelectric polymers and ferroelectric ceramics according to poling by external electric field: i) poled ferroelectric polymer, ii) certain ferroelectric materials before poling, and iii) poled ferroelectric ceramics. (c) Schematics showing the polarization directions of each composite using either ferroelectric P(VDF-TrFE) matrix or relaxor P(VDF-TrFE-CTFE) matrix with PZT particles: i) the case of normal ferroelectric polymer matrix, ii) a certain composite, iii) the case of relaxor ferroelectric matrix. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

polarization, making them suitable for high-efficiency energy-storage devices [40,41]. As a representative relaxor polymer, the chemical formula and chain structure of the P(VDF-TrFE-CTFE) terpolymer are shown at the bottom of Fig. 1a. The relaxor property can originate from polar nanoregions (the right-hand schematic in Fig. 1a), which are more easily polarized by external electric fields compared with normal ferroelectric domains [37,42]. When the electric field is removed, most of the dipoles in the polar nanoregions are randomly redistributed toward their original directions. The remnant polarization of the relaxor is therefore small, and there is almost no piezoelectric effect. Relaxor polymers may have no piezoelectric hindrance with piezoceramics during poling of piezoelectric composites. Moreover, the relaxor polymer is expected to easily align the polarizations during electrical poling due to its permittivity, but few studies of piezoelectric composite-based energy-harvesting application devices have been conducted. We therefore fabricated and compared PZT-embedded nanocomposite generators using both a normal ferroelectric P(VDF-TrFE) copolymer and a relaxor P(VDF-TrFE-CTFE) terpolymer. Fig. 1b depicts the difference in the piezoelectric response of poling between ferroelectric polymers and ferroelectric ceramics. When the external electric field was applied to a ferroelectric polymer such as P(VDF-TrFE), the polarization aligned in the opposite direction of the external electric field according to the negative longitudinal piezoelectric coefficient. On the contrary, the polarization is commonly aligned in the forward direction of the electric field in general ferroelectric ceramics such as PZT. Therefore, a composite in which the P(VDF-TrFE) matrix and the PZT filler particles were mixed had conflicting polarization directions, as shown in Fig. 1c. In this case, the opposing polarization alignments collide during poling, resulting in ineffective and cancelled net piezoelectricity of composites. However, a relaxor P(VDF-TrFE-CTFE) matrix can be effective for poling and net polarization of a PZT-embedded composite because it has almost no piezoelectricity and weak remnant polarization, which does not clash with the ferroelectric physics of PZT particles. The polar nanoregions of a relaxor matrix can therefore serve as more effective seeds for the polarization alignment of PZT particles, compared with the normal domain structure of a ferroelectric matrix (Fig. S3). The sufficient saturation

polarization, high dielectric property and low energy-loss effect of the relaxor may be also advantageous for poling an embedded PZT filler. We therefore expect that the relaxor polymer matrix is more suitable for certain piezoelectric composite devices.

Fig. 2a displays the IR spectra of a pure P(VDF-TrFE) copolymer and its composite with PZT particles, while Fig. 2b depicts those of a P(VDF-TrFE-CTFE) terpolymer and its composite. The 1177 cm^{-1} band shows the vibration absorption with C—F bonding characteristics of both fluoropolymers [43]. A peak of a polar β phase is evident at 840 cm^{-1}, as well as a peak of polar β and γ phases at 880 cm^{-1} [44]. The ratio between the peaks at 840 cm^{-1} and 880 cm^{-1} indicate that, P(VDF-TrFE) has multiple β phase regions, whereas P(VDF-TrFE-CTFE) has relatively few β phase region. The intensities at 1276 cm^{-1} and 1430 cm^{-1} have a similar tendency [43–45]. The shoulder peak of the non- polar α phase at 765 cm^{-1} appears in the IR spectra of the relaxor terpolymer, in contrast to those of the ferroelectric copolymer [44]. These IR spectra also confirm that the composite configuration with PZT nanoparticles does not affect the phase status of either fluoropolymer. Fig. 2c provides the result of XRD analyses of P(VDF-TrFE), P(VDF-TrFE-CTFE), their composites with PZT filler nanoparticles, and pristine PZT nanoparticles. The PZT particles were well synthesized, and sequentially mixed into each polymer matrix. The broad peaks of the copolymer and terpolymer below 20° are positioned at different angles. To compare them in detail, the XRD peaks between 16° and 24° are magnified (Fig. 2d). The β phase is well represented in the XRD scan of the P(VDF-TrFE) copolymer, whereas the P(VDF-TrFE-CTFE) terpolymer displays mainly an α phase

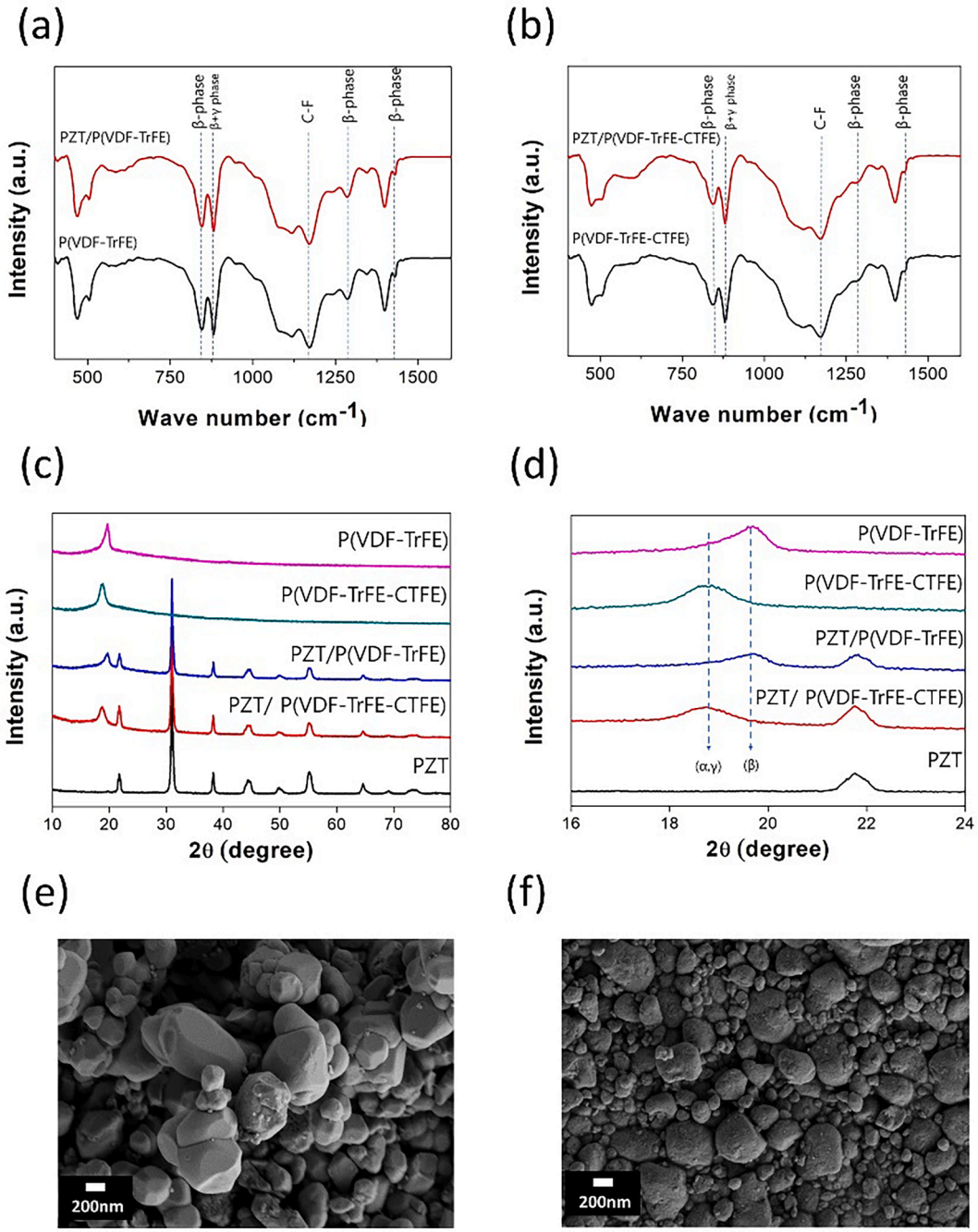

Fig. 2. IR spectra of (a) P(VDF-TrFE) copolymer and its composite with PZT nanoparticles and (b) P(VDF-TrFE-CTFE) terpolymer and its composite, respectively. (c) XRD results of P(VDF-TrFE), P(VDF-TrFE-CTFE), their composites with PZT particles, and pure PZT particles, respectively. (d) Magnified XRD peaks within the range of 16° and 24°. PZT particles after and before ball milling. SEM images of (e) non-milled PZT particles and (f) ball-milled PZT particles.

peak [43]. In both IR and XRD analyses, the ferroelectric β phase is highly evident in the P(VDF-TrFE) copolymer, but the P(VDF-TrFE-CTFE) terpolymer has only a few traces of the β phase, which indicates the terpolymer has little piezoelectricity. Rough and coarse PZT particles were ground through the ball-milling process for 24 h (Fig. 2e and f).

Fig. 3a presents the measured longitudinal piezoelectric coefficient of P(VDF-TrFE), P(VDF-TrFE-CTFE) and its composites with PZT filler particles. The d_{33} of normal ferroelectric P(VDF-TrFE) is -27 pC N^{-1} as a negative sign [46,47]. In contrast, the relaxor P(VDF-TrFE-CTFE) has little piezoelectricity with a d_{33} of -2 pC N^{-1}. Although the piezoelectric response of P(VDF-TrFE) is much higher than that of P(VDF-TrFE-CTFE), the tendency of the piezoelectricity in their composite configuration with PZT filler particles is in the opposite direction. With the poled PZT particles, the P(VDF-TrFE-CTFE) terpolymer-based nanocomposite has a d_{33} of 45 pC N^{-1}, which is larger than 24 pC N^{-1} of the d_{33} of P(VDF-TrFE) copolymer-based composite. The inversion of the sign of the d_{33} values in the composite feature is due to the high positive d_{33} of PZT (approximately 400 pC N^{-1}) [48]. This means that the piezoelectric poling efficiency of ferroelectric PZT filler is ineffective within a normal ferroelectric P(VDF-TrFE) matrix because of the opposite poling directions between the ferroelectric polymer and the ferroelectric ceramics (polarization collision). However, the ferroelectric PZT particles can be effectively poled within the relaxor ferroelectric P(VDF-TrFE-CTFE) matrix due to the dielectric property of the relaxor. This indicates that relaxor polymers can produce a greater piezoelectric coefficient for piezoelectric polymer-ceramic hybrid composites compared with a matrix of normal ferroelectric polymers. Fig. 3b depicts the dielectric properties of P(VDF-TrFE) and P(VDF-TrFE-CTFE) when used for the matrix. The relaxor terpolymer has a higher dielectric constant than do normal ferroelectric copolymers. The high dielectric constant of the matrix of piezoelectric composite is favorable for polarization alignment of embedded piezoelectric ceramic particles because the poling effect due to an external electric field is relatively easy to produce [34,36,37]. The dielectric constants were measured to be approximately 28 for P(VDF-TrFE) and 37 for P(VDF-TrFE-CTFE). The dielectric loss of both P(VDF-TrFE) and P(VDF-TrFE-CTFE) are similar, except to high frequencies. Fig. 3c depicts the dielectric property of the composite of each polymer matrix with PZT filler particles. The dielectric constants of both composites increase under the influence of PZT particles. The dielectric loss of the composites is almost same as that of a pure polymer matrix.

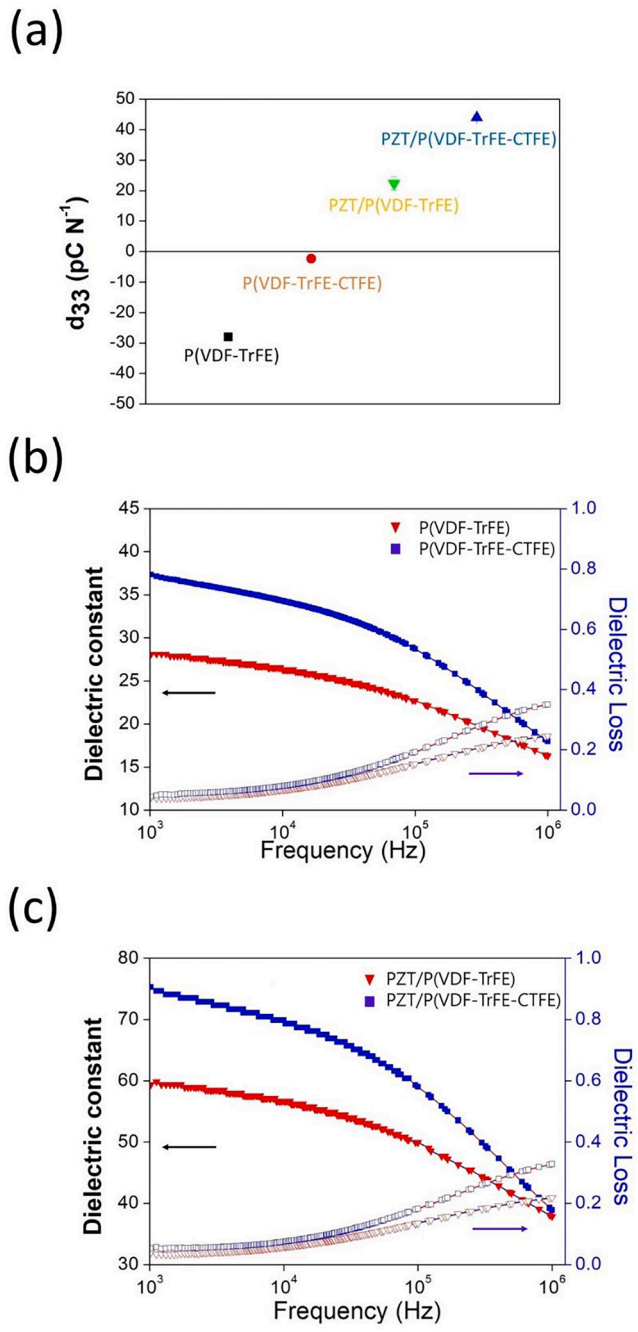

Fig. 3. (a) Measured longitudinal piezoelectric coefficients (d_{33}) of P(VDF-TrFE), P(VDF-TrFE-CTFE), their composites with PZT particles, and pure PZT particles, respectively, which can show the discrepancy between the ferroelectric PZT filler particles and the ferroelectric P(VDF-TrFE) matrix. Relative permittivity (dielectric constant) and dielectric loss of (b) P(VDF-TrFE) copolymer and P(VDF-TrFE-CTFE) terpolymer and (c) their composite configuration with PZT filler particles, respectively.

Fig. 4a presents a *P-E* hysteresis curve at 1 Hz for the normal P(VDF-TrFE) ferroelectric copolymer and its composite with PZT particles. The copolymer has a sufficiently high saturation polarization (P_s) of approximately 10 μC cm^{-2}, but that of its composite was approximately 7 μC cm^{-2}. The remnant polarization (P_r) also decreased from 7 μC cm^{-2} to 5 μC cm^{-2}. This is because of the polarization collision between P(VDF-TrFE) matrix and PZT filler particles due to their opposing dipole directions and the piezo responses during poling. In contrast, for the P(VDF-TrFE-CTFE) relaxor ferroelectric matrix composite with PZT filler, the P_s and P_r increased from 3 μC cm^{-2} to 8 μC cm^{-2} and from 2 μC cm^{-2} to 5 μC cm^{-2}, respectively (Fig. 4b). These *P-E* hysteresis curves show that relaxor polymers are more suitable that normal ferroelectric polymers in a piezoelectric composite matrix because the former have high dielectric properties and low piezoelectric responses, which are preferred for effective polarization of embedded piezoelectric ceramics. Fig. 4c presents the temperature-dependent dielectric constant of P(VDF-TrFE) and its composite with PZT particles at several input frequencies, with a linear trend indicating normal ferroelectric characteristics [4,49]. The dynamic permittivity increased until reaching the Curie temperature without the influence of input frequencies. Fig. 4d plots the temperature-dependent dielectric constant of the P(VDF-TrFE-CTFE) and its composite. The dispersed dielectric constant spectra with different maximum points depended on input frequencies, which is characteristics of typical relaxor ferroelectrics and consistent with the Volgel-Folcher law [50,51]. The overall dielectric characteristics rely on the matrix polymers while the level of dielectric constant increases with the embedding of PZT filler particles. The breakdown field of P(VDF-TrFE-CTFE) is higher than that of P(VDF-TrFE), but their composites with PZT filler particles present similar reduced breakdown fields due to the effect of the ceramic filler, as shown in the Weibull distribution of Fig. S4. Resonance peaks in the dielectric constant due to vibration of domain or dipoles means the evidence of non-ergodic relaxor ferroelectric materials. In the relaxor P(VDF-TrFE-CTFE), however, it did not

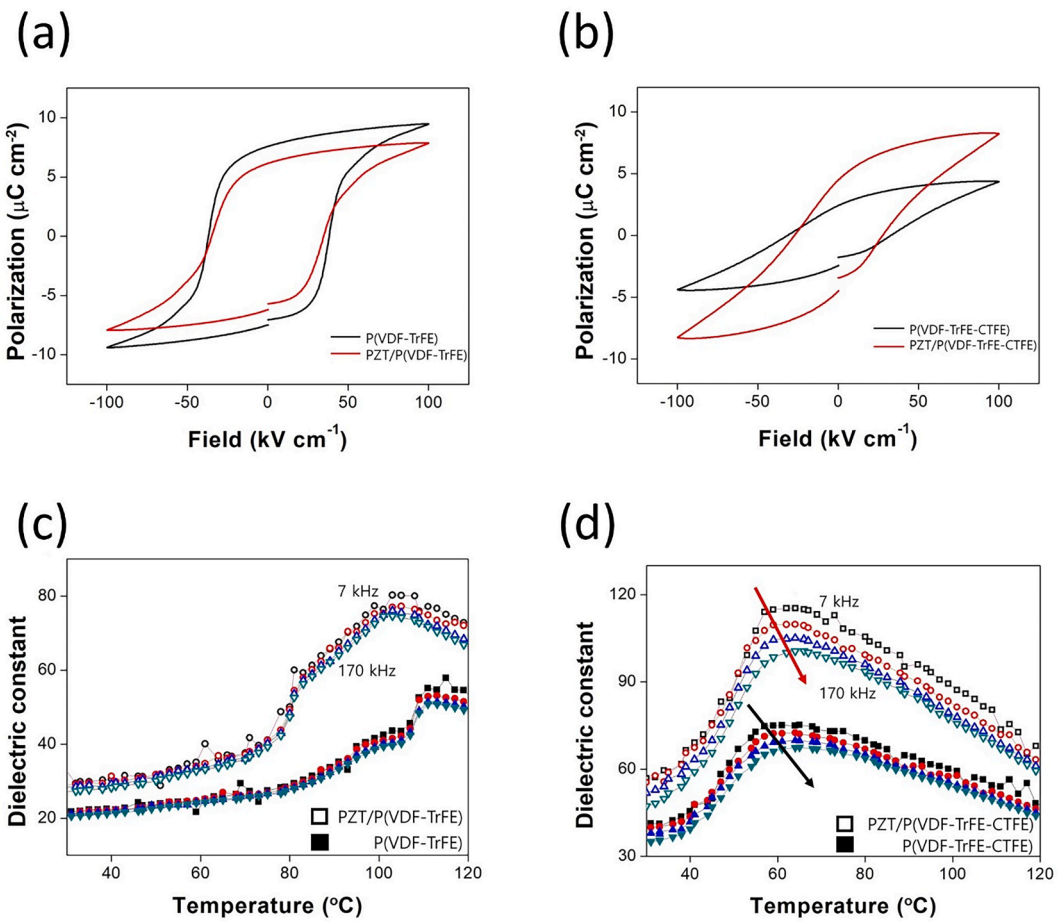

Fig. 4. *P-E* hysteresis curves (1 Hz) of (a) P(VDF-TrFE) and its composite, and (b) P(VDF-TrFE-CTFE) and its composite, respectively. (c) Temperature-dependent measurement for dielectric constant of P(VDF-TrFE) and its composite. (d) P(VDF-TrFE-CTFE) and its composite, respectively.

observe in the measurement of dielectric constant according to temperature. Therefore, we can consider that the P(VDF-TrFE-CTFE) is presumably considered the ergodic state relaxor.

Fig. 5a presents the open circuit voltage of four different piezoelectric device by bending displacement. A pure P(VDF-TrFE) energy harvester generates an output voltage of up to 30 V as the normal ferroelectric material with good piezoelectricity, whereas the pure P(VDF-TrFE-CTFE) generator provides approximately 6 V as the relaxor material with low piezoelectricity. The piezoelectric nanocomposite generators consisting of each polymer matrix and PZT filler nanoparticles were also measured. The P(VDF-TrFE) matrix of a PZT filler-based device achieved an output voltage of approximately 20 V, which is 33% lower than that of a pure P(VDF-TrFE) device. This indicates that a lower output voltage results from the polarization cancellation due to the opposing dipole alignment between a ferroelectric polymer matrix and a ferroelectric ceramic filler. In contrast, the output voltage of the P(VDF-TrFE-CTFE) matrix with a PZT filler-based generator was enhanced by up to approximately 35 V, an increasing of 300%. Fig. 5b and Fig. S5 present the voltage measurements of switching-polarity tests, which confirm that the signals of all devices are produced by piezoelectric effect. Note that the generated voltage peak is the electric potential produced by the piezoelectric device in the open-circuit state. Since the piezoelectric materials can be also considered as dielectric materials, some potential storage (capacitors) characteristics can be shown such as discharging curves with certain time width. Fig. 5c shows the short-circuit current signal of the four piezoelectric nanocomposite generators with same deformation. The P(VDF-TrFE) composite generated a lower output current (33%) compared with a pure P(VDF-TrFE) device (from approximately450 nA to 300 nA). The P(VDF-TrFE-CTFE) composite increased its output current by approximately 570% compared with a pure P(VDF-TrFE-CTFE) device (from 120 nA to 800 nA). Fig. 5d and Fig. S6 depicts the result of the switching-polarity test for current signals of all devices. The generated current signals mean the amount of charge flow throughout the connected circuit. Therefore, the area of each signal indicates the amount of charges in certain cycles. The results indicate that the relaxor ferroelectric polymer can enhance the ferroelectric polarization of ceramic fillers to improve the piezoelectric performance of composite configurations. Although some research has reported small amounts of ferroelectric ceramic particles (*e.g.*, $BaTiO_3$) can improve the piezoelectric effect of PVDF-based normal ferroelectric polymers with weak poling [52], the mechanism involved is obscure and many material types are possible. However, the opposite directions of the piezoelectric responses of ferroelectric polymers and ferroelectric ceramics were clearly defined during dipole saturation. Interactions between ferroelectric polymers and ferroelectric ceramics should therefore be further investigated with special attention paid to complex cases such as antiferroelectrics and relaxors.

4. Conclusions

We investigated the influence of polarization collision between ferroelectric polymer matrixes and ferroelectric ceramic particles which have opposing piezoelectric coefficients. Although PVDF-based polymer-ceramic hybrid piezoelectric composite devices have been studied, the interference between the polymer matrix and the ceramic particles has been neglected or rarely considered. When we used a P(VDF-TrFE) copolymer as the matrix, the total piezoelectric device performance of

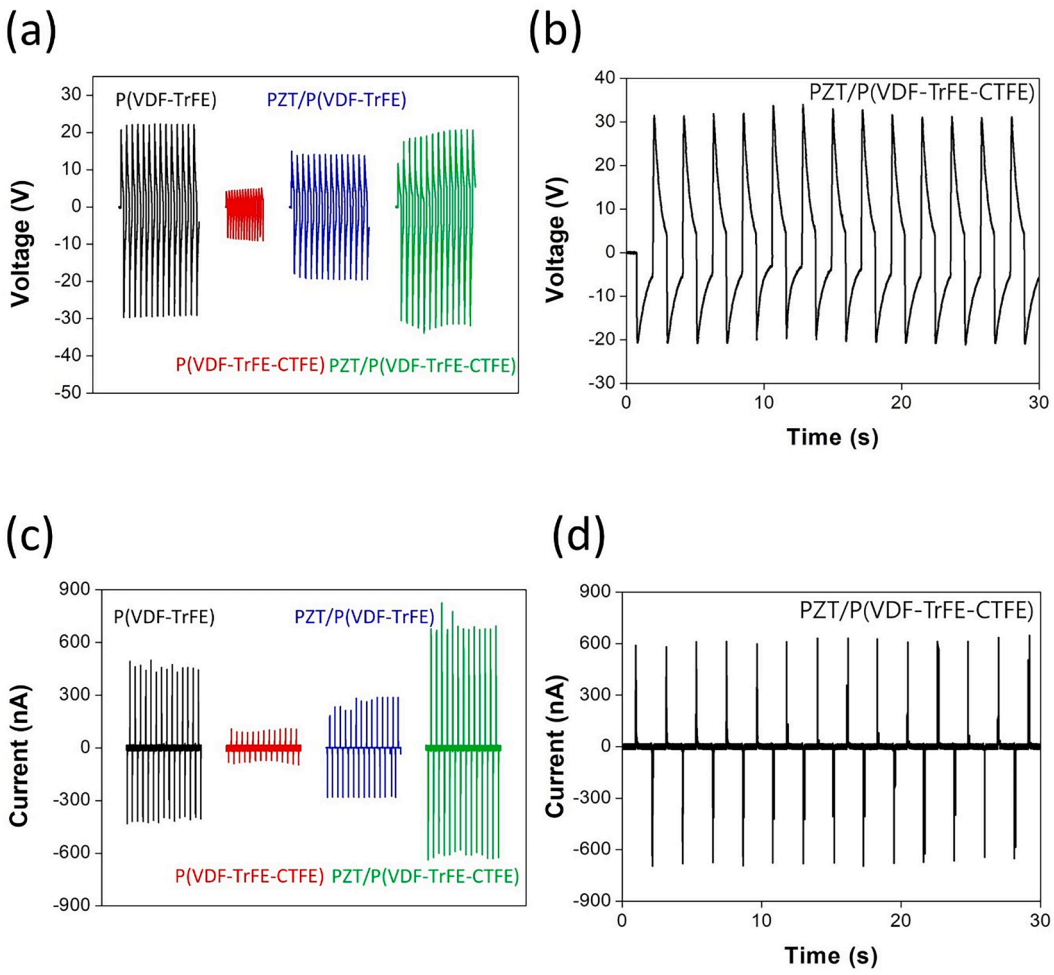

Fig. 5. (a) Generated voltage signals by energy harvesting devices consisting of pure P(VDF-TrFE), pure P(VDF-TrFE-CTFE), and their composites with PZT filler nanoparticles, respectively. (b) switching polarity test produced by the P(VDF-TrFE-CTFE) relaxor matrix-based nanocomposite generator, which shows the most efficient performance after the poling process. (c) Generated current peaks by generator devices composed of pure P(VDF-TrFE), pure P(VDF-TrFE-CTFE), and their composites with PZT filler nanoparticles, respectively. (d) switching polarity generated by the P(VDF-TrFE-CTFE) relaxor matrix-based nanocomposite energy harvester, presenting the most effective poling process.

the nanocomposite was reduced after poling. P(VDF-TrFE) has negative longitudinal piezoelectric coefficients whereas PZT particles have high positive longitudinal piezoelectric coefficients. Using a P(VDF-TrFE-CTFE) terpolymer as a matrix can therefore enhance the performance of piezoelectric nanocomposites. The P(VDF-TrFE-CTFE) terpolymer nanocomposite achieved a voltage increase of 300% and a current increase of approximately 570%. This confirms that normal ferroelectric copolymer such as P(VDF-TrFE) are poor matrixes for polymer-ceramic hybrid piezoelectric composites because of polarization collision between polymer matrixes and ceramic fillers during poling. We found that a relaxor ferroelectric P(VDF-TrFE-CTFE) terpolymer was an effective polymer matrix to help align the polarization of PZT particles because the relaxor terpolymer had a piezoelectric coefficient of nearly zero, a high dielectric response, and easily switchable polar nanoregions. To the best of our knowledge, this is the first attempt to apply a relaxor polymer matrix in flexible piezoelectric nanocomposite devices. Our results clearly suggest that the ferroelectric characteristics of polymer matrix can improve the performance of piezoelectric composite devices and applications.

CRediT authorship contribution statement

Sungbin Im: Methodology, Validation, Formal analysis, Investigation, Data curation, Visualization, Writing – original draft. **Sam Yeon Cho:** Methodology, Validation, Formal analysis. **Jae-Hyeon Cho:** Methodology, Validation, Formal analysis. **Geon-Tae Hwang:** Validation, Investigation, Resources. **Angus I. Kingon:** Resources, Funding acquisition. **Sang Don Bu:** Conceptualization, Methodology. **Wook Jo:** Conceptualization, Supervision. **Seung-Hyun Kim:** Validation, Investigation, Resources, Supervision, Project administration, Funding acquisition, Writing – review & editing. **Chang Kyu Jeong:** Conceptualization, Methodology, Validation, Investigation, Resources, Supervision, Project administration, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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