

The Effect of Crosslinker Ratio on the Performance of Piezoelectric Elastomers

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Electronic Supplementary Information

Abstract Piezoelectric elastic composites based on polydimethylsiloxane (PDMS) elastomer filled with polar phase poly(vinylidene fluoride) (PVDF) microspheres are fabricated. The regulatory role of the elastic polymer matrix structure on the performance of the composite, which is less concerned in previous studies, is explored. Here, we have elucidated that precise control of the PDMS crosslinked network governs the stress transfer mechanism, enabling rational design of high-performance piezoelectric composites. By tuning the crosslinker ratio, we achieve PDMS crosslinking densities ranging from $9.9 \times 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$ to $91.3 \times 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$, enhancing the output voltage of the piezoelectric composite with 10 wt% PVDF microsphere content from 5.3 V to 19.8 V. Finite element simulation attributes this enhancement to more efficient stress transfer within the elastomer matrix with higher crosslinking density, strengthening the dipole polarization response of polar PVDF microspheres. By increasing PVDF microsphere content to 30 wt%, the composite exhibits a piezoelectric coefficient (d_{33}) of $74 \text{ pC} \cdot \text{N}^{-1}$ and a sensitivity of $647 \text{ mV} \cdot \text{N}^{-1}$, which are 37 and 20 times higher than unoptimized composites in this work, respectively. This work advances understanding of mechanoelectrical coupling in flexible piezocomposites and provides a platform for designing next-generation sensors for intelligent robotics and non-contact acoustic sensing.

Keywords Crosslinking density engineering; Piezoelectric composite; Stress transfer mechanism; Flexible electronics

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INTRODUCTION

As a combination of flexible polymer elastomers and rigid piezoelectric materials, piezoelectric elastic composites hold great promise for applications in many fields, such as tissue engineering^[1,2] and bioelectronics^[3–9] to soft robotics,^[10–13] and energy harvesting,^[14–16] with a global market size expected to reach US\$5.929 billion by 2028. The practical performance of such composites, however, is critically hindered by the inherent mechanical mismatch between rigid piezoelectric nanofillers and compliant elastomer matrices. This modulus mismatch creates an ineffective stress transfer pathway, inducing a “stress-shielding effect” under external mechanical force: the low-modulus matrix preferentially accommodates the applied load, mechanically shielding the embedded piezoelectric fillers from the full stimulus. Consequently, efficient stress concentration at the filler-matrix interface is prevented, ultimately compromising the piezoelectric output of composite-based nanogenerators

(PENGs).^[17–19]

Conventional strategies for enhancing piezoelectric properties of composites have predominantly focused on optimizing the piezoelectric filler phase while treating the polymer matrix as a passive component. Common piezoelectric materials include zinc oxide (ZnO),^[20–22] barium titanate (BTO),^[23–25] and lead zirconate titanate (PZT).^[26] Beyond material selection, filler size critically influences dispersion and processability: micron-scale fillers allow for high loading fractions,^[27] whereas nanoscale fillers, despite their potential benefits for interfacial properties, are prone to agglomeration.^[28] To address this, surface modifiers such as polydopamine (PDA)^[29–31] and tetradecylphosphonic acid (TDPA)^[32] are commonly employed to tailor the filler-matrix interface, enhancing compatibility and thereby improving stress transfer and piezoelectric output.

Despite these efforts in filler and interface engineering, previous studies have largely overlooked how the intrinsic network structure and viscoelasticity of the elastomer matrix, particularly crosslinking density, storage modulus, and loss modulus, affect the overall piezoelectric performance. In fact, these viscoelastic characteristics represent the key physical parameters governing stress transmission from the matrix to

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the filler surface. Yet conventionally, the matrix has been treated as an ideal elastomer, in which internal stress propagates strictly along the loading direction without energy dissipation (Fig. 1a, left).^[33] This simplification, while useful, inherently neglects the molecular chain dynamics and slippage inherent to real polymer networks, where different topologies give rise to pronounced energy dissipation under dynamic loading. Consequently, enhancement strategies have been predominantly directed toward filler modification, leaving the matrix underexploited as a programmable stress-transduction medium. In reality, however, the mechanical behavior of the elastomer matrix is far more complex than the ideal elastic assumption. In polymer elastomers and their composites, the inherent anisotropy of crosslinking topology or the incorporation of functional fillers renders stress transfer inherently direction-dependent. This, combined with the intrinsic viscoelasticity of the polymer network and the coupling between energy storage and dissipation, collectively dictates the macroscopic mechanical response (Fig. 1a, right).^[34,35] Thus, engineering the network topology of elas-

tomers offers a promising route to optimize piezoelectric performance by modulating the stress transfer process. How crosslinking structure and viscoelasticity dictate stress transmission, and consequently, piezoelectric response remains largely unexplored, whereas current research has primarily focused on tailoring elastomer topology to enhance toughness.

Here, we prepared a composite system consisting of polydimethylsiloxane (PDMS) as the elastomer matrix and poly(vinylidene fluoride) (PVDF) microspheres as the piezoelectric filler. By precisely controlling the crosslinked network of PDMS, we are able to elucidate the stress transfer mechanism, which in turn enables the rational design of high-performance piezoelectric composites. By systematically varying the crosslinker ratio, the crosslinking density of the PDMS elastomer is tuned with a corresponding change in storage modulus. Finite element simulations confirm that improvement of output voltage arises from the increased stress transfer efficiency at higher crosslinking densities (Fig. 1b). Moreover, the effect of microsphere content is also explored. When the microsphere content reaches 30 wt%, the piezo-

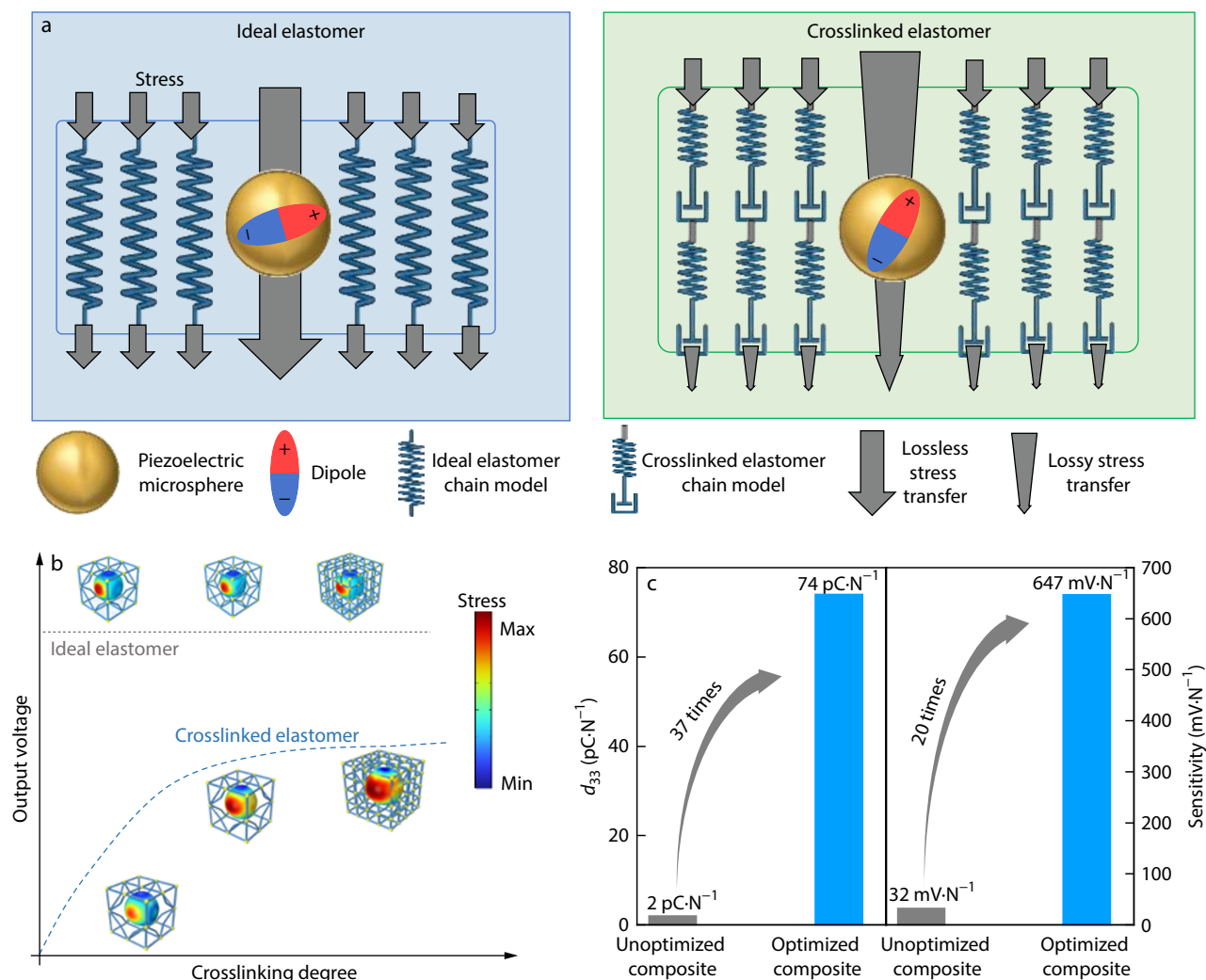


Fig. 1 (a) The contrast in stress transmission between ideal elastomer, consisted by a linear spring (left) and crosslinked elastomer, consisted by a linear spring in series with an Eyring type dashpot (right); (b) Simulated stress distribution and output voltage in ideal elastomer and crosslinked elastomer composite; (c) The comparison for d_{33} and sensitivity of piezoelectric composite before and after optimization.

electric coefficient (d_{33}) and sensitivity of the composite increased to 74 pC·N⁻¹ and 647 mV·N⁻¹ (Fig. 1c). This work establishes a mechanistic and reproducible route for flexible energy harvesters and highlights the critical, yet previously overlooked, role of polymer network topology in electromechanical coupling, which offers a new paradigm for advanced sensor and energy conversion materials.

EXPERIMENTAL

Materials

N,N-dimethylacetamide (DMAc), poly(vinyl alcohol) (PVA, $M_w=8.5\times10^5$ – 12.4×10^5 g·mol⁻¹), and PVDF ($M_w=5.3\times10^5$ g·mol⁻¹) were obtained from Sigma-Aldrich; the PDMS elastomer (Sylgard 184), consisting of a base (Part A, vinyl-terminated polydimethylsiloxane) and a crosslinker (Part B, containing a platinum catalyst, chemical structure shown in Fig. S1 in the electronic supplementary information, ESI), was purchased from Dow Corning. All chemicals were used as received without further purification.

Preparation of Polar PVDF Microsphere and Piezoelectric Composite

Polar PVDF microspheres were fabricated via a liquid-liquid phase separation approach as described in our previous work.^[36] In a typical procedure, 600 mg of PVDF and 300 mg of PVA were co-dissolved in 15 mL of DMAc under stirring. This solution was then heated to 95 °C under mechanical stirring at 400 r·min⁻¹, followed by the dropwise addition of 45 mL of PVA aqueous solution (40 mg·mL⁻¹) at a rate of 1.5 mL·h⁻¹. After complete addition, the mixture was left to stir overnight to ensure thorough phase separation. The resulting microspheres were collected via centrifugation at a speed of 8000 r·min⁻¹ and washed sequentially with 1500 mL of deionized water and 30 mL of ethanol to eliminate any residual DMAc and PVA, and approximately 375 mg of PVDF microspheres were obtained.

To enhance the crystallinity of the as-prepared microspheres, a thermal annealing process was conducted at 150 °C for 4 h, consistent with previously established protocols.^[36] The annealed PVDF microspheres were subsequently incorporated into a PDMS matrix at weight ratios of 10 wt% and 30 wt% to form composite films, and the weight ratio of crosslinker (platinum catalyst, part B) to PDMS base (part A) was set to 1:20, 1:10, and 1:5. Then, the mixture was cast into polytetrafluoroethylene molds and thermally cured at 90 °C for 4 h. After curing, the resulting piezoelectric composite films were carefully demolded for further device assembly.

Characterization

The morphology of PVDF microspheres was examined using scanning electron microscopy (SEM, Hitachi S-4700, Japan). The crystalline structure for PVDF microspheres was investigated by Fourier transform infrared spectroscopy (FTIR, Spectrum 100, Perkin-Elmer, USA) and synchrotron X-ray diffraction (XRD, BSRF-1W1A, Beijing Synchrotron Radiation Facility). Microscopic piezoelectric response of PVDF microspheres was assessed via piezoelectric force microscopy (PFM, Model MFD-3D). Specifically, the electrically biased conductive tip (NSC14 Cr/Au) of PFM is subjected to a bias current voltage of 5 V alternating current (AC) and direct current (DC) (ranging between -60 and +60 V). The piezoelectric displacement amplitude was measured via the

Radiant Precision Nano Displacement System: an AC signal is applied to the capacitor while the PFM probe contacted with microspheres, and the resultant displacement deflects the probe, changing the optical detector output. The amplitude as a function of the applied DC bias yields a butterfly-shaped curve reflecting hysteresis in dipole switching. Thermal behavior was analyzed by differential scanning calorimetry (DSC, TA Instruments Q2000) under a nitrogen atmosphere at a heating rate of 10 °C·min⁻¹. Mechanical properties were evaluated using a universal testing system (Model QTest 5), while dynamic mechanical analysis (DMA) was performed on a DMA I dynamic thermal analyzer. The Comsol software was performed for finite element simulation. The 2D representative volume element (RVE) consists of a spherical PVDF microsphere (diameter: 0.8 mm) embedded in a rectangle PDMS matrix (length × width: 50 mm × 30 mm). These settings ensure that the simulated output voltage of the high modulus composite is close to the experimental value, and the differentiation is improved among results. The simulated boundary conditions are as follows: (1) bottom center point: fixed (zero displacement); (2) top surface: uniform compressive stress of 0.1 MPa (parallel to dipole direction); (3) bottom surfaces: symmetry boundary conditions (free normal displacement); (4) mesh is set internally in the software, where the mesh is controlled by physical field, and the mesh size is a regular size; (5) material parameters: PDMS: Young's modulus (E) = 0.6, 1.2, 2.7 MPa; Poisson's ratio = 0.49 (nearly incompressible), and PVDF: piezoelectric coefficient is set internally in the software.

Fabrication and Testing of Piezoelectric Sensor

For device fabrication, the composite films were first laminated with copper tape on both sides to serve as electrodes. Poling was carried out under a DC electric field of 15 kV in silicone oil at room temperature for 1 h to orient the dipoles. Following poling, the films were annealed at 80 °C for 30 min to release any residual trapped charges.^[37] Copper wires were then attached to the electrodes using silver paste to serve as output terminals. Finally, the entire device was encapsulated with thermoplastic polyurethane (TPU) layer to ensure mechanical protection and environmental stability.

Electrical characterization was performed by applying cyclic compressive forces using a linear motor (LinMot E1100), with the resulting electrical signals recorded using an electrometer (Keithley 6517A).

RESULTS AND DISCUSSION

To isolate the effect of PVDF piezoelectric microsphere on the experimental results, we first fabricated and characterized the PVDF piezoelectric microspheres. The microspheres exhibited uniform morphology with a particle size of approximately (2.5 ± 0.9) μm, as shown in the SEM image (Fig. 2a). XRD and FTIR were used to confirm the crystal structure of the PVDF microspheres. The XRD pattern reveals two distinct diffraction peaks at $2\theta=18.50^\circ$ and 20.10° (Fig. 2b). The peak at 18.50° corresponds to the $(020)_\alpha$ or $(020)_\gamma$ crystalline phase, whereas the peak at 20.10° is assigned to the overlap of $(110)_\gamma$ and $(020)_\beta/(110)_\beta$ crystalline phases.^[38,39] The FTIR spectrum (Fig. 2c) shows no characteristic peaks of α phase (796 or 763 cm⁻¹), confirming the exclusive presence of β and γ polar phases.^[39] DSC melting curve reveals a single melting peak at 164 °C (Fig. 2d),

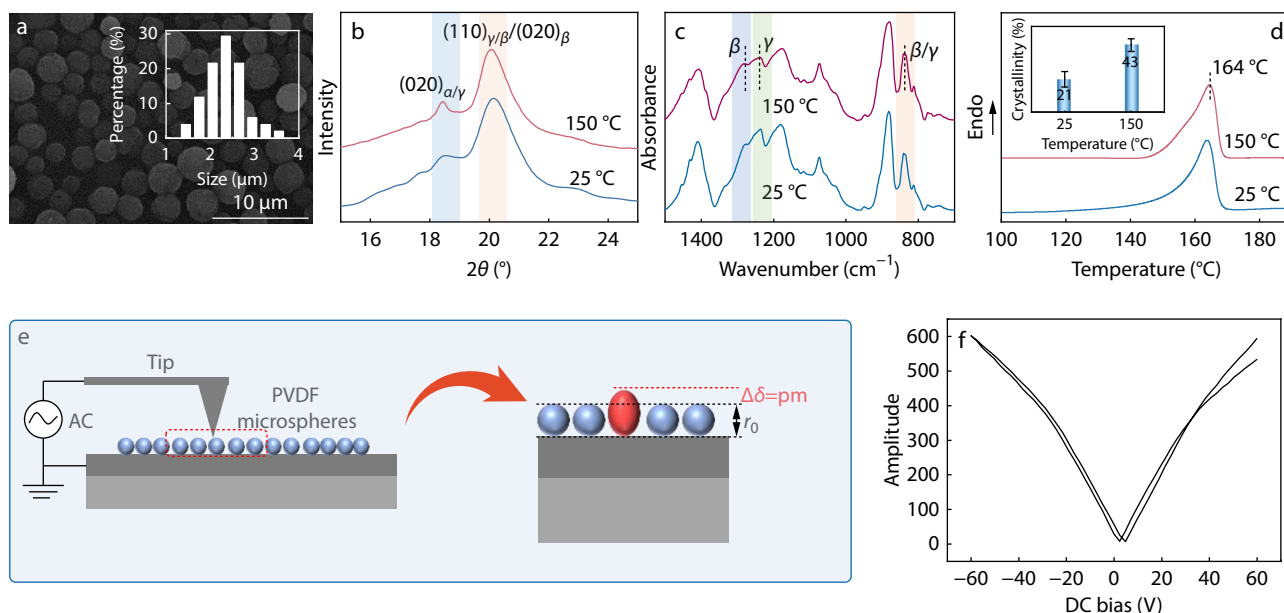


Fig. 2 (a) An SEM image of PVDF microspheres, the inset is size distribution; (b) XRD patterns, (c) FTIR spectra and (d) DSC curves of PVDF microspheres before and after annealing at 150 °C for 4 h. The inset in (d) shows calculated crystallinities; (e) Schematic diagram for PFM characterization and (f) butterfly curve of PVDF microspheres annealing at 150 °C.

which corresponds to the melting of γ phase,^[36] indicating that the PVDF microspheres predominantly consist of the γ phase, resulted from the strong polar interaction between the hydroxyl hydrogen of PVA, and H₂O and the fluorine atoms. These results confirm the successful formation of polar PVDF microspheres.

To enhance piezoelectric performance, the microspheres were annealed at 150 °C for 4 h based on previous work.^[36] After annealing, the crystal phase shows no significant variation (Figs. 2b and 2c), whereas the crystallinity increases from 21% to 43% (Fig. 2d). These results confirm the successful fabrication of piezoelectric PVDF microspheres with relatively high crystallinity.

Piezoelectric force microscopy (PFM) was utilized to assess the piezoelectric performance of PVDF microspheres, as depicted in the schematic diagram in Fig. 2(e). The effective piezoelectric coefficient (d_{33}^{eff}) is approximately 10 pm·V⁻¹ from the butterfly curve (Fig. 2f), calculated using the following Eq. (1):^[40–42]

$$d_{33}^{\text{eff}} = \frac{A}{V_{\text{tip}}} \quad (1)$$

where A corresponds to the out-of-plane deformation amplitude ($\Delta\delta$) of the PVDF microsphere surface induced by the applied electric field measured at a given DC bias point (± 60 V). V_{tip} represents the voltage on the atomic force needle ($V_{\text{tip}} = V_{\text{DC}} + V_{\text{ac}}$). Here, V_{DC} is used as a substitute for V_{tip} because it is the parameter that defines the operating point on the butterfly curve, and the $\Delta\delta$ is directly correlated with the applied DC bias in the reported measurement. The piezoelectric coefficient of prepared PVDF microspheres is higher than that of PVDF composite film (8.9 pm·V⁻¹),^[41] comparable to the piezoelectric coefficient of inorganic piezoelectric material ZnO (12 pm·V⁻¹).^[43] This result demonstrates that the fabricated microspheres exhibit piezoelectric characteristics suitable for developing piezoelec-

tric composites.

The piezoelectric composites with microspheres concentration of 10 wt% were subsequently obtained by incorporating microspheres in PDMS with different crosslinker ratios. To evaluate the influence of PDMS elastomer network structure on stress transfer, we quantitatively characterized the dynamic mechanical behavior of PDMS elastomer and its piezoelectric composites using dynamic mechanical analysis (DMA), with the results shown in Fig. S2 (in ESI). As the crosslinker ratio increases from 1:20 to 1:5, the storage modulus (E') of the PDMS elastomer increases eight-fold, from 0.18 MPa to 1.43 MPa (Fig. 3a, yellow bars, calculated from Fig. S2a in ESI). The E' value of the piezoelectric composites with a microsphere content of 10 wt% increased by a factor of 3.3, from 0.46 MPa to 1.51 MPa, as the crosslinker ratio increased from 1:20 to 1:5 (Fig. S2b in ESI). Notably, the storage modulus of piezoelectric composite is higher than that of the PDMS elastomer, and the difference in storage modulus between the composite and the matrix diminishes with increasing crosslinker ratio (Figs. S2c–S2e in ESI). Meanwhile, the loss tangent ($\tan\delta$) of the PDMS elastomer decreased from 0.58 to 0.29 over the same crosslinker ratio range (Fig. 3a, blue bars, calculated from Fig. S2f in ESI), and that of the piezoelectric composites decreased from 0.4 to 0.26 (Fig. S2g in ESI). These findings indicate that increasing the crosslinker ratio effectively enhances the rigidity of the PDMS matrix while reduces the viscoelastic dissipation, as reflected by the lower $\tan\delta$. Notably, at high crosslinker ratios, the incorporation of PVDF microspheres further increases E' and decreases $\tan\delta$, indicating that the microspheres function as a reinforcing phase.

Moreover, the crosslinking density (ν_e) of PDMS elastomer with varying crosslinker ratio was calculated by the subsequent Eq. (2):^[44]

$$\nu_e = \frac{E'}{6RT} \quad (2)$$

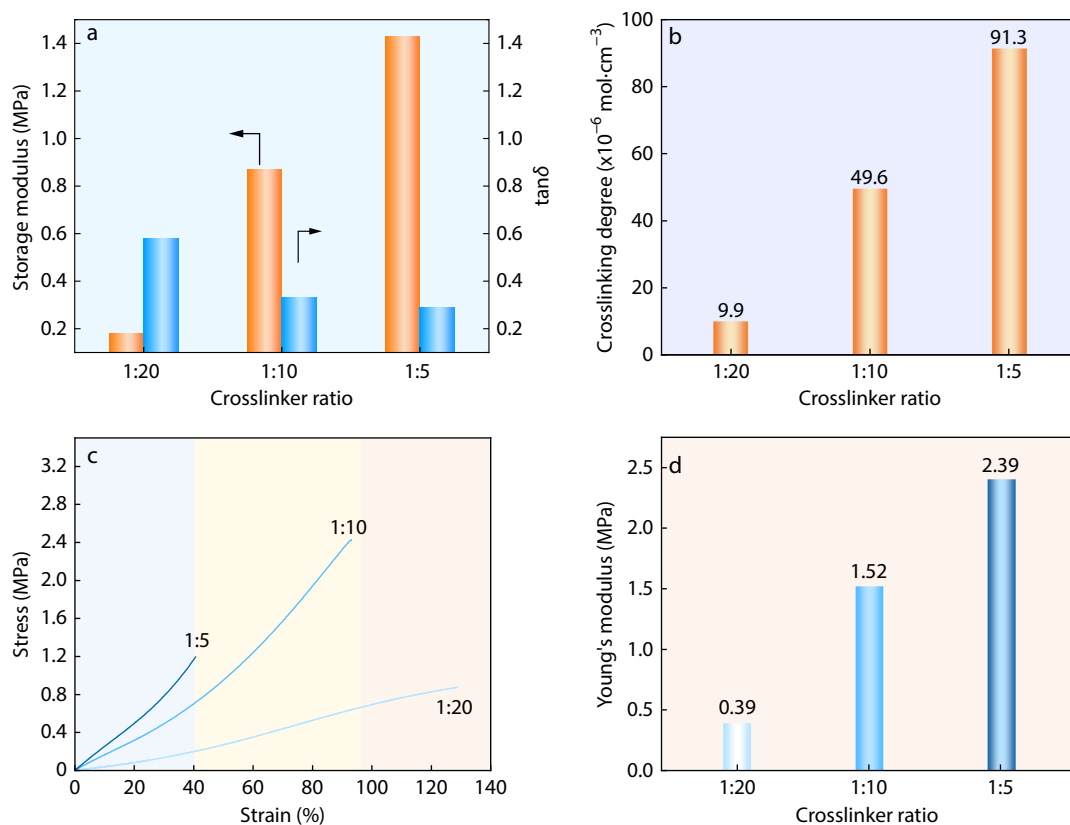


Fig. 3 (a) Storage modulus (E' , yellow bars) and loss tangent ($\tan\delta$, blue bars) of PDMS elastomers with different crosslinker ratios. The left y axis corresponds to storage modulus (unit: MPa), and the right y axis corresponds to $\tan\delta$ (dimensionless); (b) The crosslinking degree of PDMS elastomers with different crosslinker ratios; (c) Stress-strain curves of piezoelectric composites with different crosslinker ratios, and (d) the corresponding Young's modulus for piezoelectric composites.

where E' is the platform values obtained from the frequency sweep test at 30 °C (Fig. S3a in ESI); R and T correspond to gas constant and absolute temperature, respectively. The calculated crosslinking density increased from $9.9 \times 10^{-6} \text{ mol}\cdot\text{cm}^{-3}$ to $91.3 \times 10^{-6} \text{ mol}\cdot\text{cm}^{-3}$ with crosslinker ratio increased from 1:20 to 1:5 (Fig. 3b). The stress-strain behavior of the piezoelectric composites based on 10 wt% microsphere content was evaluated by tensile tests using a universal testing machine, with the representative curves shown in Fig. 3(c). As the crosslinker ratio increased from 1:20 to 1:5, the elongation at break progressively declined, reaching approximately 40% at a ratio of 5:1. The Young's modulus (E), calculated from the linear region of the stress-strain curves, increased from 0.39 MPa to 2.39 MPa with increasing crosslinker ratio (Fig. 3d). These results demonstrate that increasing the crosslinker ratio fundamentally alters the crosslinking degree of PDMS elastomer, driving a transition from a dissipative, viscous-dominated state toward a more elastic, solid-like state. With the structural parameters established, we systematically assessed the piezoelectric performance of composites fabricated with varying crosslinker ratios.

Fig. 4(a) illustrates the electromechanical conversion mechanism of the piezoelectric composite. As dictated by the law of charge neutrality, the upward spontaneous polarization (P_s) of the piezoelectric composites causes opposite surface charges to appear on each electrode, and no output signal is detected since the positive and negative charges remain balanced (Fig. 4a-I, without any force). When the piezoelectric

composite is compressed, the alignment of dipoles is disrupted, reducing the effective dipole quantity. This results in a mismatch between the initial polarization charge on the electrode and the dipole polarization. Electrons will redistribute between the two electrodes to offset the accumulated charges, restoring electrical balance (Fig. 4a-II). The open circuit voltage (V_{OC}) of the composite can be calculated using the following Eq. (3):^[45]

$$V_{OC} = \frac{Q}{C} = \frac{d_{33}\sigma}{\epsilon}h \quad (3)$$

where V_{OC} is the open-circuit voltage, Q is the induced charge, C is the capacitance in parallel, d_{33} is the piezoelectric coefficient of the piezoelectric material, ϵ is the dielectric coefficient of the piezoelectric material, σ is the vertically distributed stress on the piezoelectric material, and h is the thickness of the piezoelectric material. As shown in Fig. S3(b) (in ESI), the dielectric constant of the composite is insensitive to the variation in crosslinker ratio. Thus, under a fixed thickness, the piezoelectric output is governed by the stress on the microspheres according to the governing Eq. (3) ($V_{OC} = \frac{Q}{C} = \frac{d_{33}\sigma}{\epsilon}h$). Increasing crosslinker ratio elevates E' of composites, which improves stress transmission and is anticipated to boost the piezoelectric properties of composite (Fig. 4a-III).

Fig. 4(b) shows the piezoelectric performance of the piezoelectric composites with different crosslinking degrees under an external force of 30 N. The V_{OC} of the composites with 10

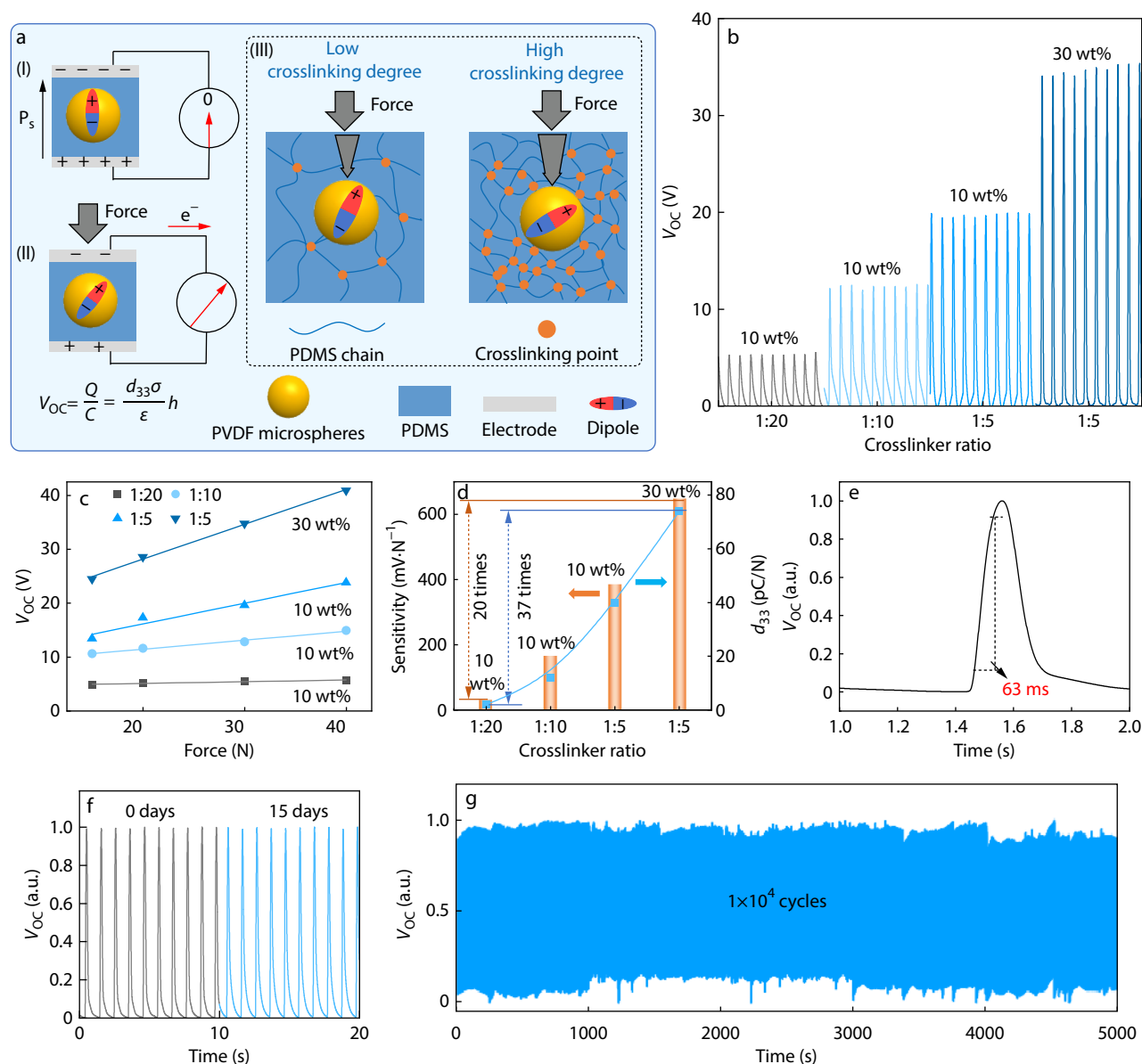


Fig. 4 (a) Schematic diagram for electromechanical conversion mechanism of piezoelectric composite (I and II) and stress transmission in composite with different crosslinking degree (III); (b) V_{OC} from PENG based on piezoelectric composites with different crosslinker ratios under external force of 30 N; (c) V_{OC} from PENG based on piezoelectric composite with different crosslinker ratios under different external forces. Symbols denote microsphere content and crosslinker ratio: $\square$, 10 wt% and 1:20; $\circ$, 10 wt% and 1:10; $\triangle$, 10 wt% and 1:5; ∇ , 30 wt% and 1:5; (d) Sensitivities (yellow bars) and d_{33} values (blue line) of PENG based on piezoelectric composites with different crosslinker ratios. The left y axis corresponds to sensitivities (unit: $\text{mV}\cdot\text{N}^{-1}$), and the right y axis corresponds to d_{33} values (unit: $\text{pC}\cdot\text{N}^{-1}$); (e) The response time of piezoelectric sensor; (f) Time stability and (g) cycle stability.

wt% PVDF microspheres increased from 5.3 V to 19.8 V as the crosslinker ratio increased from 1:20 to 1:5. Furthermore, under a fixed crosslinker ratio of 1:5, the V_{OC} value reached 35.1 V when the microsphere content is 30 wt%, which is the optimal microsphere content according to the previous work.^[36] Moreover, the forward/reverse voltage values are closed (Fig. S4 in ESI), indicating that the voltage of piezoelectric composite originates from the intrinsic piezoelectric effect rather than triboelectricity. V_{OC} and piezoelectric charge from PENG with different piezoelectric composites in this work under different external forces are shown in Fig. 4(c) and Fig. S5 (in ESI) calculated from Figs. S6 and S7 (in ESI), respectively. The sen-

sitivity for these sensors can be calculated by following Eq. (4):^[46]

$$S = \frac{\Delta V_{OC}}{\Delta F} \quad (4)$$

where ΔV_{OC} and ΔF is differences of V_{OC} and applied external force, and the d_{33} value of these composites can be calculated by $\Delta Q/\Delta F$. The sensitivities (yellow bars) and d_{33} values (blue line) for these sensors are shown in Fig. 4(d). The d_{33} and sensitivity increased significantly from 2 $\text{pC}\cdot\text{N}^{-1}$ to 74 $\text{pC}\cdot\text{N}^{-1}$, and from 32 $\text{mV}\cdot\text{N}^{-1}$ to 647 $\text{mV}\cdot\text{N}^{-1}$, respectively. The response time and stability of piezoelectric sensor based on the microsphere

composites were characterized. The sensor demonstrates a rapid response capability, with a response time of 63 ms (Fig. 4e), indicating that this piezoelectric sensor can achieve real-time response.^[47] In addition, this sensor demonstrates excellent stability. After storage for 15 days, the piezoelectric output of the composite shows negligible degradation (Fig. 4f), and the piezoelectric performance shows insignificant variation after 1×10^4 cycles (Fig. 4g).

To reveal the physical mechanism underlying the correlation between PDMS elastomer modulus (crosslinking degree) and piezoelectric properties, finite element simulation software Comsol was used to simulate the mechanical and piezoelectric properties of PVDF microsphere PDMS elastomers under different moduli. In this simulation, the 2D composite model (details shown in experimental section) was designed and an external stress of 0.1 MPa was applied parallel to the dipole direction. Conventionally, the deformation for piezoelectric materials under external forces obeys linear elastic constitutive law (Hooke's law) (Eq. 5) and electrical Eq. (6). Combining Eqs. (5) and (6), the piezoelectric characteristics of piezoelectric materials adhere to the piezoelectric constitutive equation (Eqs. 7 and 8):^[48]

$$S = sT \quad (5)$$

$$D = \epsilon E \quad (6)$$

$$S = s^E T + dE \quad (7)$$

$$D = dT + \epsilon^T E \quad (8)$$

where S is the strain of the piezoelectric material, s is the flexibility of the piezoelectric material, and T is the stress acting on the piezoelectric material; D represents the potential shift of the piezoelectric material, while ϵ and E represent the dielectric constant and electric field strength of the piezoelectric material, re-

spectively. In the absence of an electric field, the piezoelectric properties for the piezoelectric material are related to the applied stress. As can be seen from Fig. S8 (in ESI), the simulated output voltage of the composite exhibits insignificant variation with increasing PDMS modulus and remains a constant value in conventional simulation where the PDMS is regarded as an ideal elastomer, which obeys Hooke's law (Eq. 5). This result is inconsistent with the experimental results (Fig. 4b).

In reality, the PDMS elastomer employed here exhibits typical nonlinear mechanical properties (Fig. 3a). Thus, the crosslinked elastomer model used in finite element simulation also uses a Hooke's law with the same Young's modulus, but geometric nonlinearity based on the Green-Lagrange strain Eq. (9) is enabled:^[49]

$$E_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial X_j} + \frac{\partial u_j}{\partial X_i} + \frac{\partial u_k}{\partial X_i} \frac{\partial u_k}{\partial X_j} \right) \quad (9)$$

where E_{ij} represents the Green-Lagrange strain tensor, u_i and u_j denote the longitudinal and tangential displacement components, respectively, u_k denotes the longitudinal and tangential displacement components in the summation over the repeated index k , and X_i and X_j indicate the longitudinal and tangential coordinates in the initial configuration. This theory is utilized for analyzing significant deformations in nonlinear mechanical materials wherein the material remains linear elastic ($S = sT$), but the geometric nonlinearity allows the stress transfer path to change with deformation, which efficiently captures the geometric stiffening effect and supports the conclusion on nonlinear stress transfer. However, it does not account for the hyperelastic/viscoelastic nature of PDMS, thus is not suitable for large-strain or time-dependent behaviors. The simulation results of piezoelectric output for the piezoelectric composite prepared, depicted in Fig. 5(a), is based on the Green-Lagrange strain. With increasing modulus, the piezoelectric output from piezo-

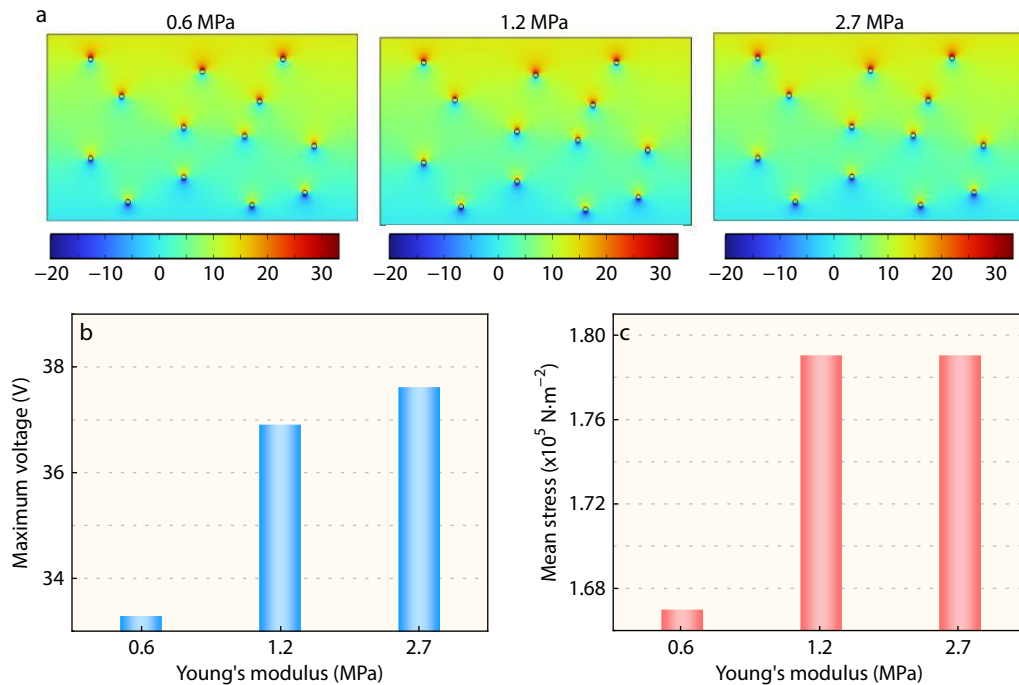


Fig. 5 (a) Simulation results of piezoelectric output for crosslinked elastomer composite, where the color bar represents piezoelectric potential in composite; (b) Simulated maximum piezoelectric output and (c) mean stress in microsphere from crosslinked elastomer composite.

electric composite gradually increases (Fig. 5b), aligning with the experimental results. The simulation results of stress distribution in crosslinking elastomer composite based on the Green-Lagrange strain is shown in Fig. S9 (in ESI). From the analysis, the mean stress in PVDF microsphere gradually increases and then stabilizes with the increasing modulus (Fig. 5c), indicating a reduction in stress loss, consistent with DMA results (Fig. 3a). This can be explained by the fact that at low crosslinking degree, stress is predominantly dissipated by the matrix, minimizing load on the microspheres and yielding low piezoelectric output. As the crosslinking degree increases, the rigidity of the composite increases. This shift directs stress toward the piezoelectric microspheres, bypassing viscous dissipation and thereby enhancing the output. This mechanistic insight bridges the gap between the mechanical properties of matrix (Fig. 3a) and the enhanced composite output. Thus, tailoring the network of elastomers effectively decreases stress dissipation of the elastomer, enhancing piezoelectric properties.

The above performance characterization results indicate that the prepared composites demonstrate outstanding

piezoelectric and mechanical properties, making them suitable for constructing piezoelectric sensors for real-time monitoring of human physiological and motor signals. A piezoelectric sensor based on the composites was attached to the wrist to detect the wrist pulse signal, as shown in Fig. 6(a). The detailed waveform (inset of Fig. 6a) exhibits the characteristic features of the pulse wave, including P1 (early systolic), P2 (late systolic), and P3 (diastolic).^[50] Moreover, the sensor was affixed to the sole to monitor different motion states, as depicted in the inset of Fig. 6(b), successfully identifying walking, running, and jumping. Furthermore, the piezoelectric sensor enables the visualization of sound signals and musical instrument identification, as illustrated in Figs. 6(c) and 6(d). Movie S1 (in ESI) visualizes the captured acoustic signals. The subsequent processing and conversion of these signals into reproducible and identifiable sound is demonstrated in the corresponding Movie S2 (in ESI). These diverse demonstrations underscore the practical benefits of the paradigm shift from filler-centric modification to matrix-topology engineering.

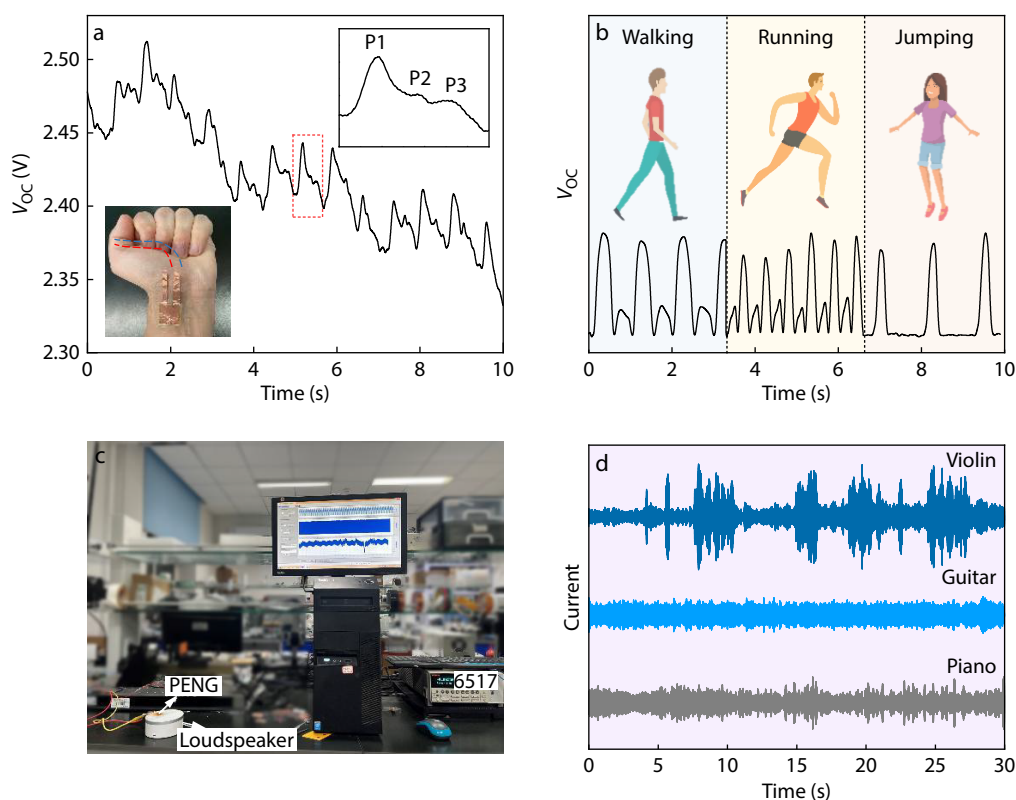


Fig. 6 (a) Pulse signal detection, the insets are the digital photo and single signal, respectively; (b) The different human motion monitoring: walking, running, and jumping; (c) The digital photo for acoustic sensing and (d) the acoustic detection of different musical instrument.

CONCLUSIONS

Flexible piezoelectric composites hold great promise for wearable electronics, but the mechano-electrical coupling dictated by elastomer crosslinking structure remains unresolved. Herein, we elucidate this dependence of electromechanical conversion for piezoelectric composite on PDMS crosslinking structure. By tailoring the curing agent concentration, we finely tuned the

crosslinking density ($9.9 \times 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$ to $91.3 \times 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$) and storage modulus (0.18 MPa to 1.43 MPa) of the PDMS matrix. Notably, increasing the crosslinking density resulted in a substantial enhancement of V_{OC} of the composite with 10 wt% PVDF microspheres, from 5.3 V to 19.8 V. Finite element simulations attribute this improvement to a significant increase in internal stress-transfer efficiency at higher crosslinking density, which in turn amplifies the dipolar polarization response of the

polar microspheres. Through optimizing microsphere content to 30 wt%, the d_{33} and sensitivity of piezoelectric composite reached $74 \text{ pC}\cdot\text{N}^{-1}$ and $647 \text{ mV}\cdot\text{N}^{-1}$, respectively, representing 37-fold and 20-fold enhancements over the unoptimized composite. Our findings offer new mechanistic insights into electromechanical coupling in flexible piezocomposites and establish a foundation for the rational design of high-performance sensors for emerging applications in smart robotics and non-contact vibration sensing.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-026-3760-0>.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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This work is dedicated to the memory of Prof. Shou-Ke Yan.

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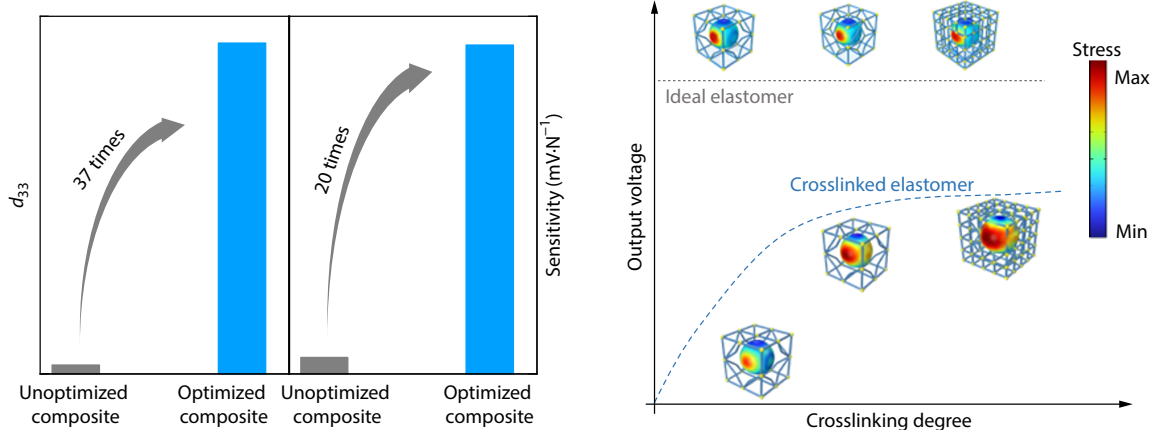
Graphical Abstract

The Effect of Crosslinker Ratio on the Performance of Piezoelectric Elastomers

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The high-performance piezoelectric composite based on poly(vinylidene fluoride) (PVDF) microsphere-polydimethylsiloxane (PDMS) elastomer was successfully fabricated through adjusting crosslinking degree of PDMS. Finite element simulation attributes this enhancement to more efficient stress transfer within the elastomer matrix with higher crosslinking density, strengthening the dipole polarization response of polar microspheres.



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