Largely Enhanced Energy Harvesting Performances of DEG by Constructing All-Organic Dielectric Composites with Soft and Deformable Filler

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Part I: Detailed calculation process of energy density

Based on the theory of energy storage of planar capacitor ($Q_2=C_2U_2=Q_1=C_1U_1$), the generated electrical energy (ΔE) during one generation cycle can be expressed from Equation (S1):

$$\Delta E = \frac{1}{2}C_2U_2^2 - \frac{1}{2}C_1U_1^2 = \frac{1}{2}C_1U_1^2\left[\frac{C_1}{C_2} - 1\right]$$

(S1)

where Q, C and U represent the charge, the capacitance and the bias voltage applied on the DE, and the subscripts 2 and 1 represent the released state and stretched state of the DE film, respectively. Meanwhile, the DEG can be considered as a variable planar capacitance, thus its C can be calculated through Equation (S2):

$$C = \frac{\varepsilon_0\varepsilon_r S}{d}$$

(S2)

where ε_0 is the permittivity of vacuum, ε_r, S and d refer to the dielectric constant, area, and thickness of the DE film, respectively. Substituting Equation (S2) into Equation (S1), the rewritten expression of ΔE can be obtained:

$$\Delta E = \frac{\varepsilon_0\varepsilon_r S_1}{2d_1}U_1^2\left[\frac{S_1d_2}{S_2d_1} - 1\right]$$

(S3)

According to the principle of volume constancy ($S_2d_2=S_1d_1$) applied, thus Equation (S3) can be rewritten as:

$$\Delta E = \frac{\varepsilon_0\varepsilon_r S_1}{2d_1}U_1^2\left[\left(\frac{S_1}{S_2}\right)^2 - 1\right]$$

(S4)

Finally, the mass energy density (w, the ratio of the ΔE to DEG material's mass ($m=\rho S_1d_1$) can be predicted:

$$w = \frac{\varepsilon_0\varepsilon_r S_1}{2md_1}U_1^2\left[\left(\frac{S_1}{S_2}\right)^2 - 1\right] = \frac{\varepsilon_0}{2\rho d_1^2}\varepsilon_r U_1^2\left[\left(\frac{S_1}{S_2}\right)^2 - 1\right]$$

(S5)

Therefore, the mass w can be succinctly described as Equation (S6):

$$w \propto \frac{\varepsilon_r U_1^2}{\rho}\left[\left(\frac{S_1}{S_2}\right)^2 - 1\right]$$

(S6)

$$w \propto \frac{\varepsilon_r U_1^2}{S3}\left(\frac{S_1}{S_2}\right)^2 - 1\right]$$

Part II: Characterization methods

¹H-NMR Spectroscopy: The ^1H NMR spectra were performed on a 600 MHz instrument of the Bruker AV600 NMR spectrometer produced in Germany, and $CDCl_3$ was used as the solvent.

Fourier transform infrared spectroscopy (FT-IR): The structural analysis of LBR and LEBR were characterized by Fourier transform infrared spectroscopy (Tensor 27, Bruker Optik, Germany) from 4000 to 500 cm^{-1} in transmission mode with a disc of KBr.

Gel permeation chromatography (GPC): The weight-average molecular weight (M_w) was measured by gel permeation chromatography (GPC) on a Waters Breeze instrument equipped with three Waters columns (Steerage HT3_HT5_HT6E) by using THF as the eluent (1 mL/min) and a Waters 2410 refractive index detector. A polystyrene standard was used for calibration.

Scanning electron microscope (SEM): SEM (S-4800, Hitachi, Japan) was employed to observe the morphologies of the TiO_2/PMVS composites and GEBR/PMVS composites by the mode of secondary electron (SE) imaging and backscattered electron (BSE) imaging, respectively. Before the observations, the GEBR/PMVS composites were polished at -140 °C by using a cryo-ultramicrotome (Leica EM UC7, Germany), and the TiO_2/PMVS composites were freeze fractured in liquid nitrogen to expose a cross section that contains TiO_2. The dispersed size of the GEBR phase in GEBR/PMVS composites was analyzed using Image-Pro Plus 7, a professional 2D image analysis software.

Atomic force microscope (AFM): A Bruker Multi Mode AFM with a Nanoscope IV controller in Quantative Nanomechanical Mapping (AFM-QNM) mode was used to measure the nanomechanical properties of composites. Before conducting observations, the samples were precut into small strips with dimensions of 5 cm in length and 1.0 mm in width. Two lines perpendicular to the stretching direction were marked on the surface of each sample, allowing for precise calculation of the strain

based on the measured distance between these lines. Next, the samples were subjected to pre-stretching to achieve a specific strain and were then secured onto a homemade stretching sample platform, as shown in Figure S1. The holder used for this purpose had a diameter of 1 cm and a height of 5 mm. To ensure a smooth surface, a steel rod with a diameter of 0.3 mm was placed at the center of each sample. The cryo-ultramicrotome (Leica EM UC7, Germany) was used at an extremely low temperature of -140 °C to perform the cutting process. The cut was made parallel to the stretching direction, minimizing the influence of surface roughness on the observations. For each sample, a minimum of five measurements were conducted, and one representative image is provided here for each sample.
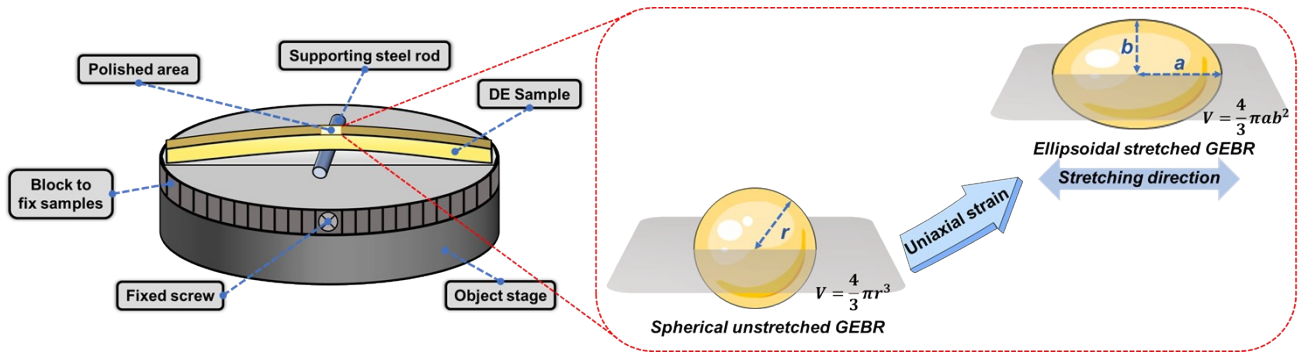

Figure S1. Homemade stretching sample platform for AFM measurements.

Assuming the volume of GEBR remains constant before and after the stretching of samples, and GEBR is always a regular sphere, the volume of GEBR can be expressed as Equation (S7).

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi a b^2$$

(S7)

Where r is the radius of spherical unstretched GEBR filler, a and b are the major axis and minor axis of ellipsoidal stretched GEBR. Thus, r can be expressed in terms of a and b, as Equation (S8).

$$r = \sqrt[3]{ab^2}$$

(S8)

Then, the strain of GEBR (ε_{GEBR}) along the stretching direction of the samples can be defined as:

$$\varepsilon_{GEBR} = \frac{a-r}{r} \times 100\%$$

<div align="right">(S9)</div>

After substituting Equation (S8) into Equation (S9), ε_{GEBR} can be rewritten as:

$$\varepsilon_{GEBR} = \left[\left(a/b \right)^{\frac{2}{3}} - 1 \right] \times 100\%$$

<div align="right">(S10)</div>

Mechanical properties: The tensile tests and cyclic stress-strain tests of the samples were performed on dumbbell-shaped samples (length × width × thickness:20 × 4× 0.5 mm³) using a tensile apparatus (Instron 5567, USA) at room temperature with a tensile rate of 500 mm/min. The elastic modulus of the samples was determined by the slope of the stress-strain curve at 10% strain. For the cyclic stress-strain test, the sample was stretched to a constant strain of 200% and then carried out loading process without relax time at same speed.

Dielectric properties: The dielectric properties of the samples were measured by a broadband dielectric spectrometer (BDS, Concept 40, Novocontrol GmbH, Germany) over a frequency range from 10^{-1} Hz to 10^{6} Hz at room temperature. The samples used for the measurements had a diameter of 10 mm and a thickness of 0.5 mm.

Electrical conductivity: A high resistance meter (GEST-121, Beijing Guance, China) was used to measure the electrical conductivity (EC) of samples, which is the reciprocal of volume resistivity. The electrical conductivity (EC) was calculated by using the following equation:

$$EC = \frac{4L}{R_v \pi d^2}$$

<div align="right">(S11)</div>

where L is the thickness of the sample, R_v is the resistance of the sample and d is the diameter of the sample.

Electric breakdown strength (E_b) and bias breakdown voltage under uniaxial strain (U_{1b}): The E_b and U_{1b} was measured by a home-made equipment. Conductive carbon grease was coated onto

both sides of the annular DE film as compliant electrodes. The dimension of working area of DE film was $80\times20\times0.5$ mm^3. A linear motor (E1100, Linmot Co. Ltd.) was used to stretch the DE film (600 mm/min) and record the uniaxial strain. The voltage was supplied by a high-voltage direct current generator (DTZH-60, Wuhan Dotek Electric) under a ramp rate of 1 kV/s until electric breakdown.

Energy harvesting performance: The energy harvesting performance of the samples was evaluated according to the previous report using a set of instruments including oscilloscope, high voltage source, tensile machine, and a pair of clamps, as shown in Fig. S5(b). Conductive carbon grease was coated onto both sides of the annular DE film as compliant electrodes. The dimension of working area of DE film was $80\times20\times0.3$ mm^3. The capacitance of sample under different uniaxial strains was measured and recorded by a Digital Multimeter (DMM6500, Tektronix, USA). C_P is parallel transfer capacitors in the circuit as a protective role for avoiding electrical breakdown, which is usually set as 1.3 times of C_1. Both diode and resistance are used to protect circuit. The initial prestrain of as-prepard samples and VHB 4905 is set as 50% and 100%, respectively, because the former has better elasticity than the latter. The input mechanical energy (W_{mech}) and the change of voltage across DE film are recorded by force sensor and oscilloscope, respectively.

The DEG energy harvesting process or lighting up LEDs process was carried out through the following four steps: (i) stretching process: uniaxial stretching was performed on the DEG subassembly under a constant speed of 600 mm/min by using a linear motor from released state to stretched state; (ii) boosting process: close all the switches, make the DC source with preset input voltage U_1 charge the DE film and C_P for 5 s, and observe the brightness of the LEDs; (iii) releasing process: open all the switches, and release the DEG subassembly under a speed of 600 mm/min to the released state; (iv) harvesting process or lighting up LEDs process: close switch S_2 and switch S_3

to make the DEG and C_P discharge the LEDs as well as the oscilloscope record output voltage U_2, and observe the brightness of the LEDs. Thus, the mass w can be calculated by Equation (S12):

$$w = \frac{1}{2m}[(C_2 + C_P)U_2^2 - (C_1 + C_P)U_1^2]$$

(S12)

where C_1, C_2, U_1, U_2 represents the capacitance of DE film under stretched and released state, the input bias voltage and output voltage, respectively.

The full-life energy density (w_{FL}) of DEG can be roughly calculated by Equation (S13). It is assumed that the w of DE decreases linearly with the increase of fatigue times.

$$w_{FL} = \frac{1}{2}(w_{max} + w_{min}) \times N_{FL}$$

(S13)

where w_{max} and w_{min} represents the maximum energy density obtained at the 1st generation cycle and that obtained after the N_{FL} (fatigue life) times generation cycle under certain strain, respectively.
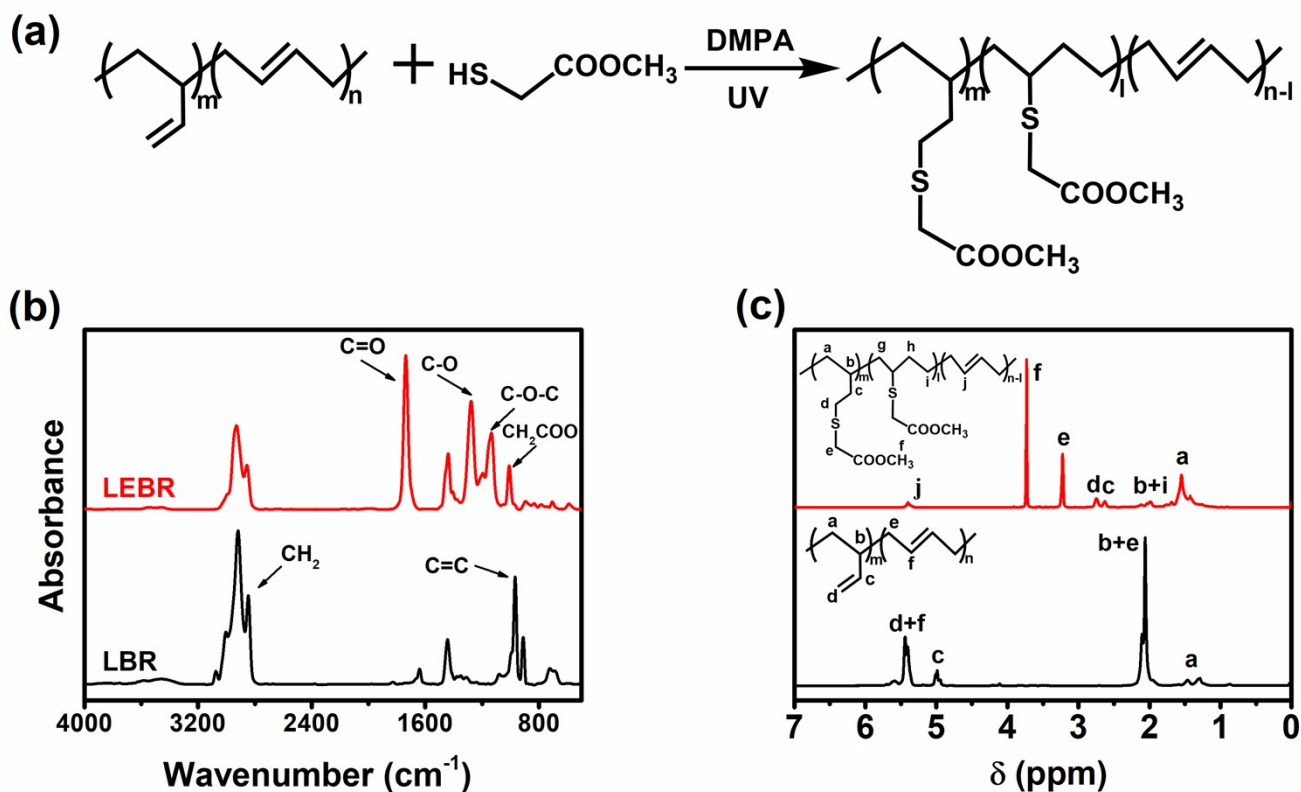
Part III: Figures and Tables

Figure S2. (a) Synthetic mechanism of LEBR;
(b) FTIR spectra and (c) ^{1}H NMR spectra of LBR and LEBR.

The FTIR spectra of LBR and LEBR is shown in Fig. S2(b). The characteristic peaks at 969 cm^{-1} and at 2919 cm^{-1} of LBR represent the C=C and CH$_2$, respectively. The new characteristic peaks at 1738 cm^{-1}, 1280 cm^{-1}, 1140 cm^{-1} and 1010 cm^{-1} of LEBR represent the C=O, C-O, C-O-C and CH$_2$COO stretching modes, respectively, demonstrating the grafting of ester groups on the LBR chain.

The ^{1}H NMR spectra was used to further determine the grafting degree of ester group, and the results are shown in Fig. S2(c). The characteristic peaks at 1.46, 5.00 and 5.44 ppm in the spectrum of LBR represent the chemical shifts of -CH_2- in the backbone of 1,2 butadiene units, -CH=CH$_2$ and -CH=CH_2 in the side chain of 1,2 butadiene units, respectively. After the thiol-ene reaction, both characteristic peaks at 5.00 and 5.44 ppm disappear, and two new strong peaks at 3.13 and 3.65 ppm

appear on the spectra of LEBR, representing the chemical shift of -SCH_2COO- and -COOCH_3, which indicates that the 1,2-vinyl double bonds have been fully reacted by thiol groups, and ester groups have been introduced into the molecular chain of LBR. More importantly, the peak at 5.40 ppm that represents the chemical shift of C-CH=CH-C from 1,4 butadiene units does not completely disappear, and these residue double bonds can promote both the self-crosslinking of LEBR and co-crosslinking between GEBR and PMVS.
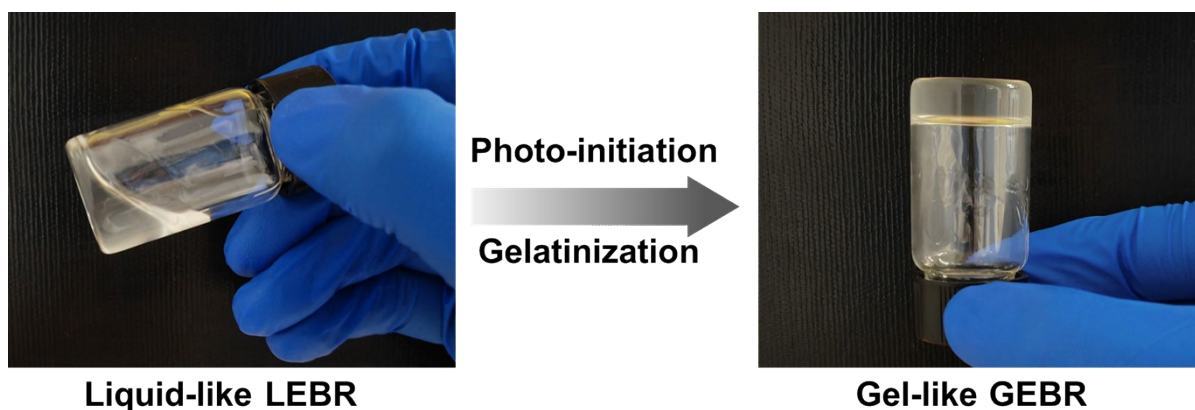

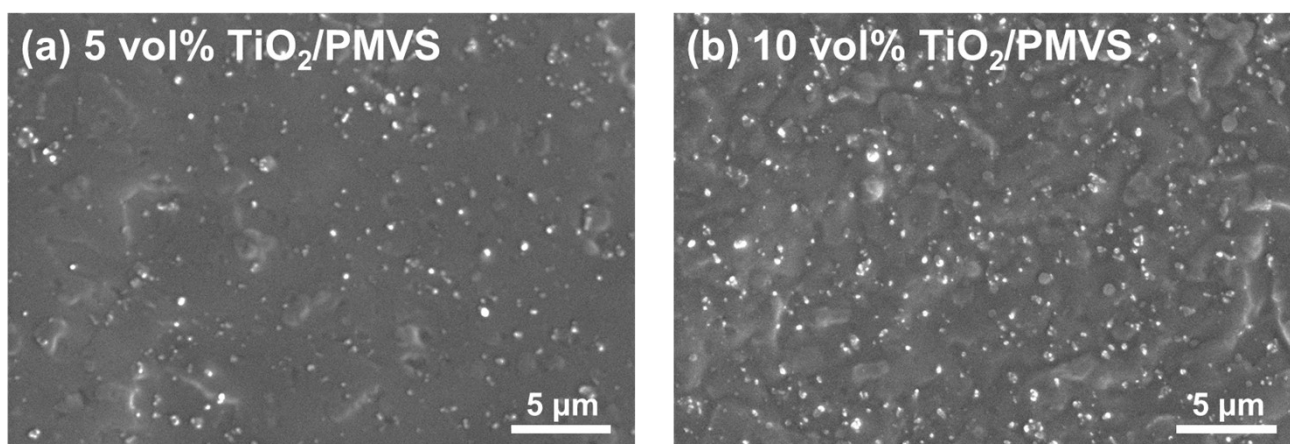**Figure S3.** The state of LEBR and GEBR at room temperature.

Figure S4. SEM micrographs of (a) 5 vol% and (b) 10 vol% TiO$_2$/PMVS composites.
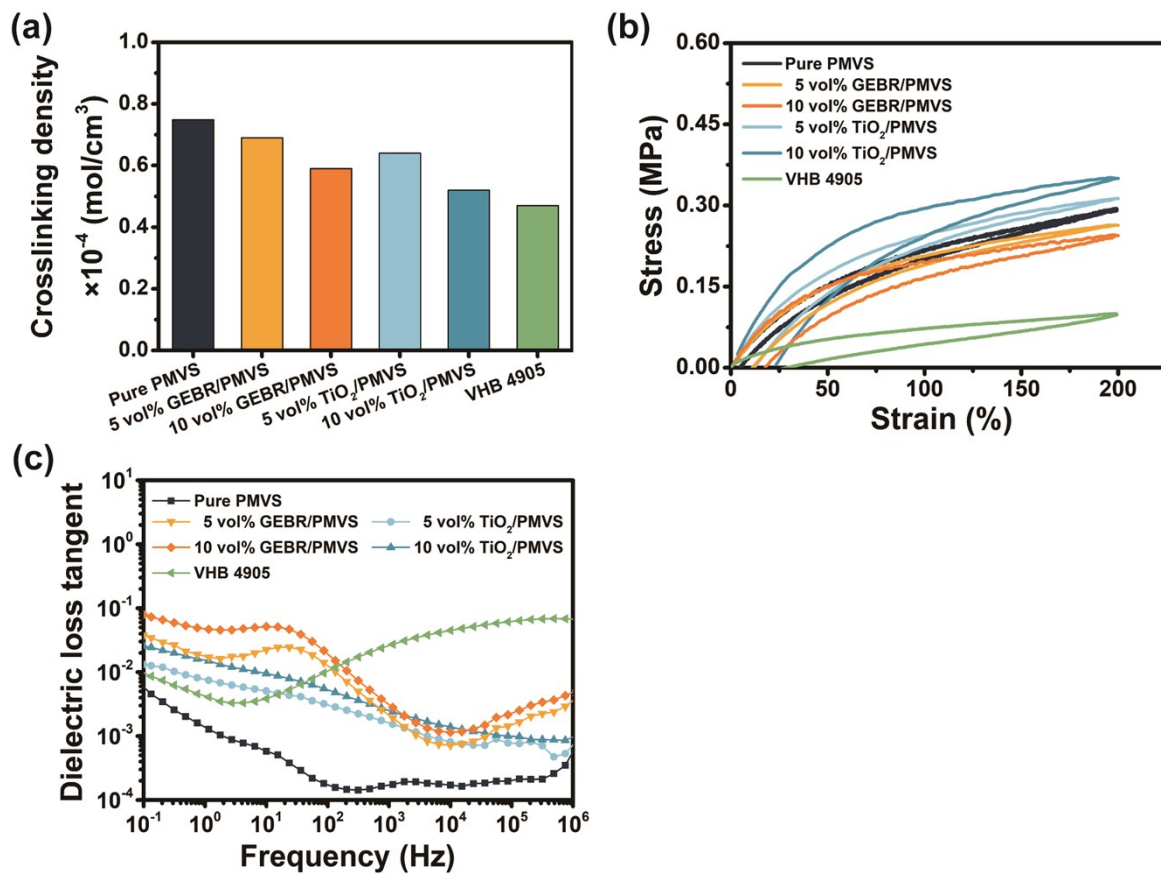
Figure S5. (a) Crosslinking density, (b) cyclic stress-strain curves and (c) dielectric loss tangent versus frequency of all the samples.
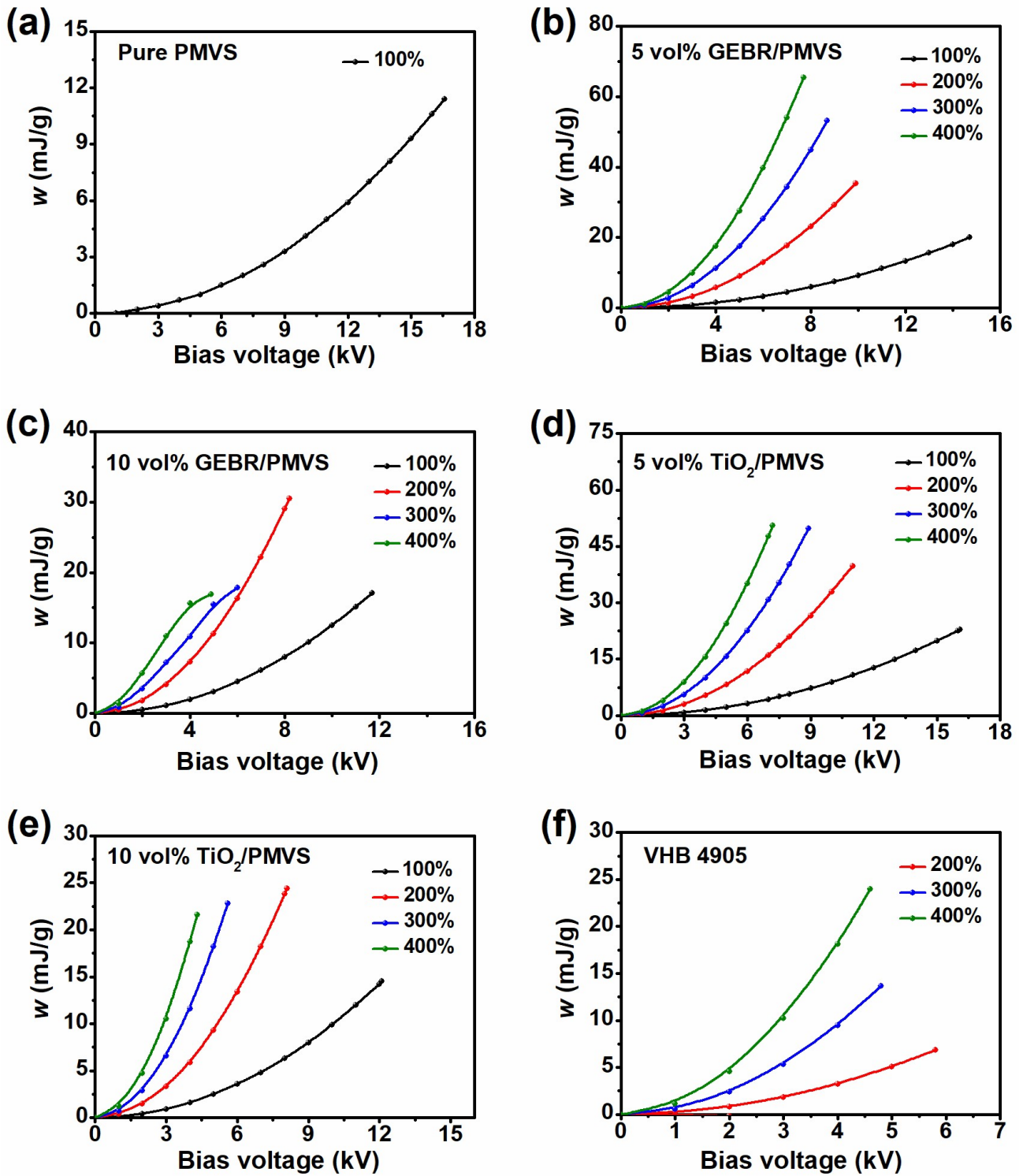
Figure S6. Energy density versus bias voltage under different uniaxial strain of all the samples.
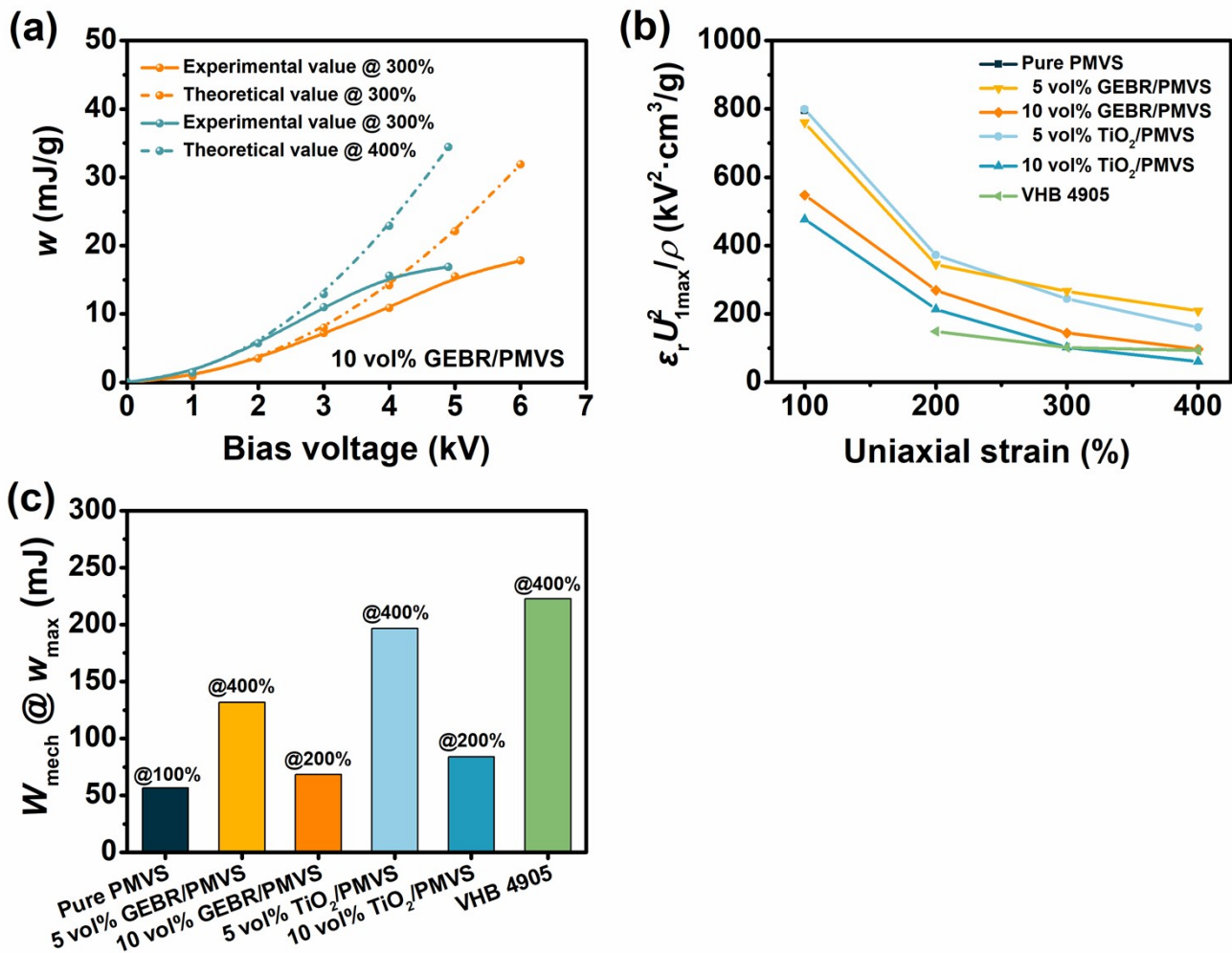
Figure S7. (a) Experimental values and theoretical values of w of 10 vol% GEBR/PMVS composite under 300% and 400% uniaxial strain; (b) $\varepsilon_r U_{1max}^2/\rho$ versus uniaxial strain and (c) W_{mech} under the condition of obtaining the w_{max} of all the samples.
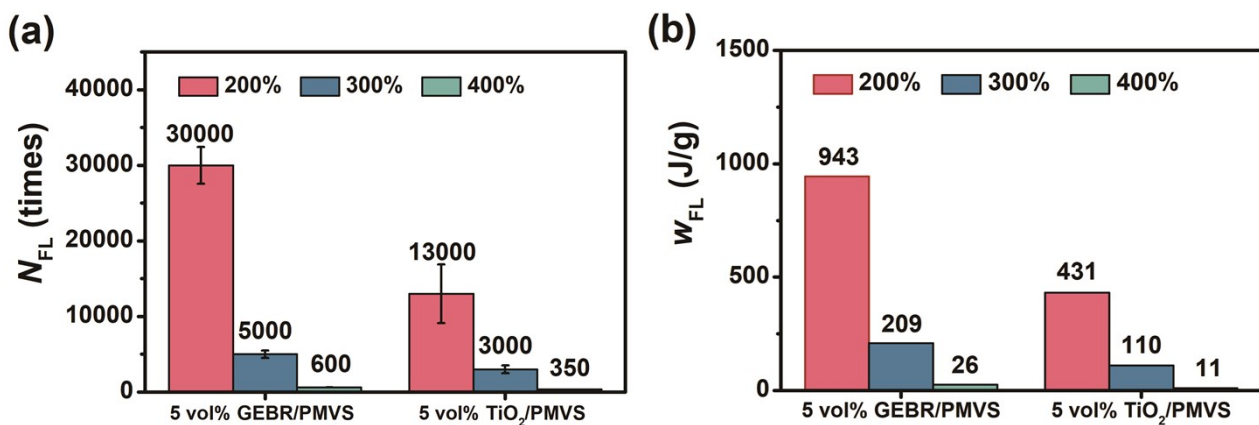

Figure S8. (a) N_{FL} and (b) w_{FL} under 200%, 300% and 400% cyclic uniaxial strain of 5 vol% GEBR/PMVS composite and 5 vol% TiO$_2$/PMVS composite.

Table S1 The formulation of preparing PMVS dielectric composites. [a]

Samples	PMVS (g)	GEBR (g)	TiO$_2$ (g)	DCP (g)
Pure PMVS	100	0	0	1
5 vol% GEBR/PMVS	100	5	0	1
10 vol% GEBR/PMVS	100	10	0	1
5 vol% TiO$_2$/PMVS	100	0	21.3	1
10 vol% TiO$_2$/PMVS	100	0	42.6	1

a The ρ of TiO$_2$ and GEBR is 4.26 g/cm^3 and 1.00 g/cm^3, respectively.

Table S2 Mechanical properties, dielectric properties and density of all the samples.

Samples	Elastic modulus (MPa)	Tensile strength (MPa)	Tensile stress at 300% (MPa)	Elongation at break (%)	ε_r @10^{-1} Hz	EC (S/cm)	Density (g/cm^3)
Pure PMVS	0.38	0.37 ±0.02	0.35	361 ±30	2.80	2.50×10^{-15}	0.97
5 vol% GEBR/PMVS	0.27	0.55±0.11	0.32	686±36	3.41	6.85×10^{-15}	0.97
10 vol% GEBR/PMVS	0.22	0.66±0.10	0.28	990±48	3.88	2.54×10^{-14}	0.97
5 vol% TiO$_2$/PMVS	0.41	0.79±0.16	0.38	738±46	3.42	3.51×10^{-15}	1.11
10 vol% TiO$_2$/PMVS	0.47	1.69±0.21	0.43	1024±52	3.94	5.92×10^{-15}	1.21
VHB 4905	0.21	0.88 ±0.09	0.11	1268 ±32	4.27	1.90×10^{-15}	0.97