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Flexible PET/EVA-based piezoelectret generator for energy harvesting in harsh environments

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ABSTRACT

Stable and repeatable operation is paramount for practical and extensive applications of all energy harvesters. Herein, we develop a new type of flexible piezoelectret generator, which converts mechanical energy into electricity consistently even under harsh environments. Specifically, the generator, with piezoelectric coefficient (d33) reaching ~ 6300 pC/N, had worked stably for continuous ~ 90000 cycles, and the generator pressed by a human hand produced load peak current and power up to ~ 29.6 μA and ~ 0.444 mW, respectively. Moreover, the capability to steadily produce electrical power under extreme moisture and temperature up to 70 °C had been achieved for possible applications in wearable devices and flexible electronics.

1. Introduction

With the rise of intelligent wearable electronics, energy harvesters converting ambient mechanical energy into electricity have attracted much attention, which is not only because the energy source (e.g., human body movement, airflow, sound vibration, water waves etc.) ubiquitously exists in ambient background and is free, but also because the converting energy could enable these electronics to be functional indefinitely, thereby reducing the dependence on battery power [1–3]. Recently, flexible generators based on different working mechanism mainly including piezoelectric [4,5], electromagnetic [1,6] and electrostatic effect [3,7–17] have been successfully demonstrated with typical applications in mobile health care [8,13], human-machine interaction [9,14], wireless communication [15] and self-charging cells [10,11], etc. Among these generators, flexible electrostatic generators like triboelectric generators [3,7–12] and electrictet generators [13–17], have obtained more interests due to their simple fabrication process, high conversion efficiency and environmentally friendly without chemical processing. However, the output properties and stability of these generators are mainly determined by the surface surplus charges [15,18,19], which will be neutralized, once exposed to the moist air atmosphere, impairing the output performance of generators [20–22]. Thus, well encapsulation of these electrostatic generators is required to endure long-term exposure to harsh environments. Previously, Guo et al. demonstrated a water-proof triboelectric generator that could be driven by the water flow [23], and Lee et al. had developed a fully packaged triboelectric sensors array for mapping the distribution of foot produced pressure [24]. However, the additional packaging material would add volume and reduce the flexibility of the generators [15,20]. New strategy with minimum packaging materials and low impact on the flexibility should be considered for flexible generators operating under harsh environments.

Flexible piezoelectret, known of high piezoelectric coefficient (d33), light-weight and low-cost, etc, has extensive transducer applications, such as energy harvesters [25–28] and loudspeakers [29]. Since the electric dipole-like charges are produced inside the materials [25], the piezoelectret generators, one kind of electrostatic generators, have the potential to be excellent energy harvester candidates that still can perform well in harsh environments. In this work, we present a new type of flexible piezoelectret generator based on the polyethylene terephthalate (PET) electret film and the ethylene vinyl acetate copolymer (EVA) adhesive layer via a hot-pressing method. The corona charging technique was used to generate megascopic electric dipoles inside a big air bubble of the generator. Mechanical push and release the generator will change the dipole moments of the electric dipoles and alter the electrostatic induction intensity to generate alternating electricity, with d33 coefficient reaching ~ 6300 pC/N and stable outputs for continuous ~ 90000 operations. Experimentally, the

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generator pressed by a human hand produced load peak current and power up to ~ 29.6 μA and ~ 0.444 mW, respectively. Moreover, the most prominent advantage of this generator is the remarkable output stability under harsh environments of extreme moisture and temperature up to 70 °C, indicating that the generator may be suitable for wearable energy harvesting and used in other harsh environments.

2. Results and discussion

2.1. Fabrication of the flexible PET/EVA-based piezoelectret generator

The detailed fabrication steps of the flexible PET/EVA-based piezoelectret generator are schematically given in Fig. 1a and Fig. S1. The raw material was the flexible ~ 45 µm-thick PET electret film with the ~ 25 µm-thick and ring-shape EVA adhesive layer at the boundary, which was defined as the EVA/PET laminated film (Fig. 1b). The cross-section view scanning electron microscope (SEM) image (Fig. 1c) clearly shows the EVA/PET laminated structure. The surface morphology of the PET electret film was investigated by atomic force microscope (AFM), indicating the PET surface roughness varied from ~ 82 to ~ 78 nm (Fig. S2). In theory, the rough surface morphology is helpful to capture more surplus charges. The charges capturing ability of the PET electret film was studied via the corona charging method [15], as indicated in Fig. S3. In this work, two PET electret films were charged with positive and negative high voltages (values of 20 and −20 kV), respectively, and then the corresponding surface potential versus time curves were measured (Fig. 1d). It’s found that the surface potential for positive and negative charging still maintained at about 0.52 and −0.50 kV after 50 days, respectively. These results indicate that the PET electret film is an excellent electret material, with the ability to capture and maintain both positive and negative surplus charges for a long time.

The fabrication steps began with fixing four polydimethylsiloxane (PDMS) spacers (size of 0.5×0.25 cm², thickness of 1 mm) on four corners of the EVA/PET laminated film (Fig. S1-I and Fig. S4a). Subsequently, another EVA/PET laminated film placed at the top was bonded to the laminated film with spacers via a hot-pressing method (Fig. 1-I, Fig. S1-II), forming the PET/EVA/PET laminated film with an arch-shaped air bubble with the height of ~ 1 mm (Fig. S4b). The cross-section view SEM image indicates that the two EVA/PET laminated films were bonded tightly (Fig. 1e). Moreover, the PET/EVA/PET laminated film could stand the shearing force up to ~ 33 N/cm² before separation, indicating the strong mechanical bonding characteristics (Fig. 1f).

The as-fabricated PET/EVA/PET laminated film was then corona charged, in order to generate megascopic electric dipoles inside the air bubble (Fig. S1-III) [26]. In the next step, aluminum (Al) adhesive tape (thickness of ~ 100 µm) was covered on two outside surfaces of the charged PET/EVA/PET laminated film (Fig. S1-IV), forming the PET/EVA/PET laminated film with an arch-shaped air bubble with the height of 0.5–1 mm (Fig. S4b). The cross-section view SEM image indicates that the two EVA/PET laminated films were bonded tightly (Fig. 1e). Moreover, the PET/EVA/PET laminated film could stand the shearing force up to ~ 33 N/cm² before separation, indicating the strong mechanical bonding characteristics (Fig. 1f).

The as-fabricated PET/EVA/PET laminated film was then used to generate megascopic dipoles inside the air bubbles, forming a PET/EVA-based flexible electret generator with effective area of about ~ 4×4 cm² (Fig. 1-II and Fig. 1g).

2.2. Working mechanism of the PET/EVA-based flexible piezoelectret generator

By virtue of the megascopic electric dipoles inside the air bubbles, piezoelectret materials have the piezoelectric-like property as the
traditional piezoelectric materials, similar to lead zirconate titanate (PZT), zinc oxide (ZnO) and polyvinylidene fluoride (PVDF), etc [25,30,31]. Herein, the corona charging method was used to generate electric dipoles inside the air bubble of the PET/EVA/PET laminated film before the two electrodes were added on the outer surfaces, as shown in Fig. 2a. Specifically, high voltage up to \(-20\) kV was applied on the corona needle for about 3 min, with samples placed about 5 cm below the needle tip. Under the strong electric field intensity, the air in the air bubble was broken down to generate ionic charges with both polarities. The positive and negative ionic charges were driven by the electric field, and captured by the upper and lower inner PET surfaces, respectively. As a result, the air bubble with charged PET inner surfaces worked as megascopic electric dipoles.

The short circuit thermally stimulated discharge (TSD) method was employed to verify the existence of electric dipoles (Fig. 2b). Specifically, our laminated film and PET raw film were corona charged first, and then two outer surfaces were covered by Al electrodes. The samples were heated in a thermal chamber with a temperature rising rate of \(3^\circ\)C/min, and the induced current curves were recorded \(\text{in-situ}\) by an electrometer. If there are electric dipoles, measurable electrical current peak in the heating process can be measured. As indicated in Fig. 2b, the measured current curve of the PET/EVA/PET laminated film consisted of a current peak started at about \(70^\circ\)C and ended at about \(110^\circ\)C, with the maximum peak value located at about \(90^\circ\)C. The influences from the potential shape changes of the air bubble were negligible as no visible output currents were measured before \(70^\circ\)C. In comparison, no significant current peak was observed in the short circuit TSD current curve of the PET raw electret film.

To measure the quasi-static piezoelectric \(d_{33}\) coefficient, a generator was operated by a give force \(F\) and the corresponding short-circuit output current was recorded (Fig. 2c). The value of transferred charges \(Q\) was achieved by integrating the current over time (Fig. 2d), and the \(d_{33}\) coefficient can be calculated [26]:

\[
d_{33} = \frac{Q}{F}
\]

The \(d_{33}\) coefficient of our generator reached \(\approx 6300\) pC/N, which was significantly larger than that of generators based on traditional cellular polypropylene (PP) piezoelectret film (Fig. 2c) [26,32]. This outstanding piezoelectric property is attributed to the excellent charges capturing ability of PET electret and low elastic modulus of the air bubble structure. Moreover, the stability of \(d_{33}\) coefficient was investigated by placing the generator in indoor atmosphere for weeks and it...
maintained in a narrow range around the original value for 6 weeks, as indicated in Fig. 2c.

Based on above piezoelectric-like behavior, Fig. 2d schematically illustrates the power generating processes of the generator. At any states, the megascopic electric dipoles will generate induced charges on the top and bottom Al electrodes, and the charge density on the electrode (σe) is decided by the following equation [27]:

$$\sigma_e = -\varepsilon_0 E \left( \frac{\varepsilon}{\varepsilon_0} + \varepsilon \right)$$

(2)

where $\varepsilon_0$ and $\varepsilon$ are the dielectric constant of air and relative dielectric constant of PET, respectively. $E$ is the electric field in the PET layer and $\sigma_0$ represents the charge density captured by the PET inner surface. $D_1$ is the thickness of PET layer and $D_2$ is thickness of air bubble or the dipole moments of the megascopic electric dipoles. In our case, $\varepsilon_0$, $\varepsilon$, $E$, $\sigma_0$, and $D_1$ are constants, and $\sigma_e$ is affected by $D_2$.

Fig. 2d-f show a non-sinusoidal excitation (hand pressing motion) of the generator with the resulting open-circuit voltage response and short-circuit current response. In the original state (Fig. 2d-I), the electrical potential between the two electrodes are in equilibrium state, and no open-circuit voltage or short-circuit current can be observed (Fig. 2e-I and Fig. 2f-I). When the generator is compressed (Fig. 2d-I to III, during the very short state II), $D_2$ decreases and the charge densities on the top and bottom electrodes also decrease. The open circuit voltage curve increases in the whole compressing process (Fig. 2e-I to III). The short circuit current curve increases to positive peak value (Fig. 2f-I to II) and then drops to zero (Fig. 2f-II to III), resulting a sharp positive current peak. As the compression state maintains (Fig. 2d-III), a new equilibrium is established. The open-circuit voltage keeps at the highest value (Fig. 2e-III) and the short circuit current keeps at zero (Fig. 2f-III). It is noted that most of the surplus charges will not be neutralized when the two PET layers are contacted with each other, which is benefit by the rough surface morphology of the PET (Fig. S2). If the generator is released (Fig. 2d-III to I, during the very short state IV), $D_2$ increases because of the mechanical elasticity of the generator. The charge density on both electrodes will increase. The open-circuit voltage drops from highest value to zero (Fig. 2e III to I). The short circuit current increases to negative peak value (Fig. 2f-III to IV) and then drops to zero (Fig. 2f-IV to I), resulting a sharp negative current peak. At last, the electrical potential between the two electrodes become in equilibrium state again.

In general, the basic working mechanism of the generator is the electrostatic induction effect caused by the megascopic electric dipoles. Compressing and releasing the generator will change the dipole moments of the electric dipoles. Thus, the electrical potential between the two electrodes are changed, and the alternating electricity is generated. Switching polarity tests were also carried out to confirm that the measured output signals are generated from the generator rather than from the artifacts of the measurement system (given in the right side of Fig. 2e and f).

### 2.3. Electrical output properties of the flexible PET/EVA-based piezoelectret generator

The electrical outputs of the flexible PET/EVA-based piezoelectret generator were carefully investigated by periodically compressing and releasing at controlled pressure and sinusoidal frequency. Typically, the generator was attached to a force meter, which was tightly fixed onto an x-y-z mechanical stage.

By virtue of the large piezoelectric $d_{33}$ coefficient, the output properties of our generator were excellent. Under given applied pressure of 6.67 kPa and sinusoidal frequency of 5 Hz, the load peak current and power density of the generator with different external

![Fig. 3. Electrical outputs of the flexible PET/EVA-based piezoelectret generator. (a) Load peak current and power density of a generator with respect to different load resistances, under given applied pressure of 6.67 kPa and sinusoidal frequency of 5 Hz. (b) Load peak current and transferred charge density for a generator with respect to different applied pressure and frequency of 6.67 kPa and 5 Hz. (c) Load peak current and transferred charge density for a generator with respect to given applied pressure of 6.67 kPa and different applied frequency. (d) Load peak current and transferred charge density for a generator with continuous operations of 90000 cycles, under given applied pressure and frequency of 6.67 kPa and 5 Hz.](image-url)
resistors were measured (Fig. 3a). The maximum load peak power density reached ~ 25.923 μW/cm², when the corresponding load peak current density and load resistance were ~ 0.241 μA/cm² and 60 MΩ, respectively. It should be noted that unless otherwise specified, the load resistance is 60 MΩ for optimal outputs for the prototype system.

The load peak current density and corresponding transferred charge density (Δσ) for the generator under given applied frequency of 5 Hz and different applied pressure is given in Fig. 3b. It’s found that when the applied pressure was less than 1.33 kPa, the load peak current density increased approximately linearly. As the applied pressure increased to be higher than 1.33 kPa, the load peak current density increased approximately linearly too, with a smaller increasing rate. The variation tendency of the Δσ was similar to that of the load peak current density, which was divided to two regions. These output behaviors are similar to the “vertical contact-separation mode triboelectric generator” [33]. The load peak current density and Δσ reached ~ 0.239 μA/cm² and ~ 6.648 nC/cm², respectively, when the applied pressure reached 6.67 kPa. By continuously increasing the applied pressure, the peak current and corresponding transferred charge density of our generator tended to be saturated, as the air bubble was completely compressed.

Furthermore, the load peak current density and Δσ increased step by step under given applied pressure of 6.67 kPa and different applied frequency, from ~ 0.077 μA/cm² at 1.2 Hz to ~ 0.237 μA/cm² at 5 Hz. However, the Δσ almost kept at a constant value of ~ 6.650 nC/cm² for different applied frequency (Fig. 3c). According to the above results, the load peak current density of the generator is related to both of the applied pressure and frequency, and the Δσ is only related to applied pressure.

The output stability performance of the generator was studied by pressing and releasing for continuous ~ 90000 cycles, under given applied pressure and frequency of 6.67 kPa and 5 Hz, respectively. As indicated in Fig. 3d, both of the load peak current density and Δσ remained at the constant values of ~ 0.245 μA/cm² and ~ 6.645 nC/cm². This remarkable stability performance is attribute to the excellent charges capturing ability of PET electret and good flexibility and elasticity of the generator.

2.4. Stability of the flexible PET/EVA-based piezoelectret generator under harsh environments

As the megascopic electric dipoles exist inside the flexible PET/EVA-based piezoelectret generator and the electrodes are well protected, this generator has the great potential in harvesting mechanical...
energy under harsh environments. The stability of the generator under extreme moisture environment was investigated. Specifically, the generator was placed into a closed space full of water vapor and continuously operated under given applied pressure of 6.67 kPa and sinusoidal frequency of 5 Hz, respectively (Fig. S7). Typical load current curves generated by the generator in one second were recorded for every 5 min (Fig. 4a). The load peak current density varied between ~ 0.256 μA/cm² and ~ 0.268 μA/cm² for the whole 25 min of measurement. Moreover, the generator was soaked into water (Fig. 4b), and 6 blue LEDs connected in series were lit up by hand pressing the generator (Fig. 4c and Video 1). The turn-on threshold voltage of the 6 blue LEDs was ~ 15 V (Fig. S8) and the highest peak current went through the LEDs was ~ 29.6 μA (Fig. 4d). Therefore, the generator generated an instantaneous output power of ~ 0.444 mW. Above results indicated that our generator had the outstanding ability in converting the mechanical energy into electricity under the extreme moisture environment or even completely immersed in water.

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In comparison, an arch-shaped flexible generator (insert in Fig. 4e) based on PET electret film was also operated under the high water vapor environment. In this case, the surplus charges contacted with extreme moisture directly. The load peak current density dropped from ~ 0.197 μA/cm² to ~ 0.0185 μA/cm² after continuously operating for 10 min. Then, the generator was only operated for 3 s at each 5 min time interval after removing the vapor, the output current of the generator could not recover again (Fig. 4e).

The output performance of the flexible PET/EVA-based piezo-electret generator under different temperatures was characterized. A heater was used to control the temperature of the generator, which was continuously operated under the applied pressure and frequency of 6.67 kPa and 5 Hz (Fig. S9). As given in Fig. 4f, when the temperatures increased from 30 °C to 70 °C, the load peak current density only had relatively stable outputs between ~ 0.251 μA/cm² and ~ 0.263 μA/cm². If the temperature was then kept at 70 °C for 25 min, the output currents remained stable. However, higher temperature can cause the loss of the megascopic electric dipoles inside the generator based on the short circuit TSD measurement result (Fig. 2a). As such, the output performance of the generator would reduce (Fig. S10).

3. Conclusions

In summary, a new type of flexible piezoelectric generator based on EVA/PET laminated film was fabricated, in which megascopic electric dipoles were captured inside the air bubble. By changing the dipole moments of the electric dipoles, the generator converted mechanical energy into electricity effectively, with δ<sub>d</sub> coefficient reaching ~ 6300 pC/N. Specifically, load peak current and corresponding peak power of ~ 29.6 μA and ~ 0.444 mW were reached by hand pressing the generator, and stable outputs were achieved for ~ 90000 continuous working cycles. More importantly, the generator had remarkable output stability under harsh environments with extreme moisture and temperature up to 70 °C, indicating the feasibility for wearable energy harvesting. This study provides a new, simple and efficient strategy for designing robust and reliable flexible energy harvesting devices.

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Appendix A. Supporting information

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