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Tunable Buckled Beams with Mesoporous PVDF-TrFE/SWCNT Composite Film for Energy Harvesting

Zhe Xu¹, Yin Liu¹, Lin Dong¹, Andrew B. Closson¹, Nanjing Hao¹, Meagan Oglesby², Gladys Patricia Escobar², Sidan Fu¹, Xiaomin Han¹, Chunsheng Wen¹, Jifeng Liu¹, Marc David Feldman², Zi Chen^{1,*}, and John X.J. Zhang^{1,*}

¹Thayer School of Engineering, Dartmouth College, Hanover, NH 03755, United States

²Schools of Medicine, University of Texas Health Science Center, San Antonio, TX 78229, United States

Abstract

By incorporating mesoporous piezoelectric materials and tuning mechanical boundary conditions a simple beam structure can significantly take advantage of limited mechanical displacements for energy harvesting. Specifically, we employed a mesoporous PVDF-TrFE composite thin film mixed with single wall carbon nanotubes to improve the formation of the crystalline phase in this piezoelectric polymer. The film was then patterned on a thin buckled beam to form a compact energy harvester, which was used to study the effects of two boundary conditions, including the end rotation angle and the location of a mechanical stop along the beam. We carefully designed controlled experiments using mesoporous PVDF-TrFE film and PVDF-TrFE/SWCNT composite films, both of which were tested under two cases of boundary conditions, namely, the rotation of the end-angle and the addition of a mechanical stop. The voltage and current of the energy harvester under these two boundary conditions were respectively increased by approximately 160.1% and 200.5% compared to the results of its counterpart without imposing any boundary conditions. Thereby, our study offers a promising platform for efficiently powering implantable and wearable devices for harnessing energy from the human body which would otherwise have been wasted.

ToC Figure

*Corresponding author: John X.J. Zhang, John.Zhang@dartmouth.edu Zi Chen, Zi.Chen@dartmouth.edu.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. The SEM image of un-dispersed single-wall carbon nanotube (SWCNT) in the mesoporous PVDF-TrFE/CNT composite film and the transmission electron microscopy (TEM) image of the SWCNT bundle; the X-ray image of the lead deformation pattern in dog's heart; the thermal properties of PVDF-TrFE/CNT composite material; the FTIR spectra acquired from porous PVDF-TrFE film and porous PVDF-TrFE/SWCNT composite film respectively; the strain analysis from theoretical simulation in the angle rotation situation; the curvature profile of the deformed beams for different pin locations, d obtained from the FE simulation; the basic components of the experimental apparatus.

Keywords

piezoelectricity; composite material; beam structure; energy harvesting; low mechanical inputs

Introduction

In recent years, with the rapidly increasing demand of implantable medical devices, a number of researchers have been concentrating on developing new sustainable power systems in order to increase the longevity of biomedical devices such as implantable cardioverter defibrillators (ACIDs). This popular topic mainly stems from the fact that the capacity of currently used batteries cannot suffice the total power consumption necessity of these devices, thereby resulting in the need for additional surgery to replace the battery every 5-7 years. Also, the components of batteries are normally hazardous and thus inhospitable to biological systems. The concept of implantable energy harvesting has thus attracted significant attention because it can scavenge mechanical energy, e.g., physical displacements from vital organs (i.e., the heart), and then convert it to useful electrical power. Hence, developing battery re-charging mechanisms is desirable for these life-saving biomedical devices.¹⁻³ Even though a wide range of materials can be employed in the implantable energy harvesting field,⁴⁻⁷ piezoelectric polymers, especially PVDF and its co-polymer PVDF-TrFE, stand out among others because of their excellent energy conversion efficiency, fabrication with minimum technical difficulty, and most importantly, superior bio-compatibility.⁸⁻¹³ Recently, driven by the prominent potentials in biomedical applications, the study of piezoelectric polymers has made significant progress.^{14,15} For example, *Wang et al.* fabricated the sponge-like piezoelectric polymer film by the etching of Zinc Oxide (ZnO) nanoparticles. When the film was excited by the acoustic wave at 40Hz it produced an open-circuit voltage and short-circuit current up to 11V and 9.8μA, respectively.¹⁶ With the effort of the Khatua group, the highest voltage and current from the self-poled PVDF/AlO-rGO flexible nanocomposite can respectively reach 36.03V and 0.79μA, when triggered with approximately 24.39N contact force.¹⁷ Without any doubt, the piezoelectric polymer does have a strong capability to generate a high level of electric power.

Unfortunately, based on the current research progress, if greater voltage and current outputs from the piezoelectric polymer or its composite materials are expected, higher mechanical inputs, such as larger contact force and higher working frequency must be adopted. It is not evident to conclude that aforementioned types of materials can guarantee their electrical output when the working frequency is relatively low (less than 2Hz) and the physical displacement from the vital organ, such as the heart, is not large enough (approximately 3mm to 5mm). In this work, we are focusing on developing novel mesoporous PVDF-TrFE composite material mixed with the single wall carbon nanotube, and further integrating and modifying the boundary conditions imposed on the conventional beam structure energy harvester to increase its strain deformation along the beam.

As shown in Figure 1(A), one of key processes for the thin film formation is spincoating.¹⁸ Prior to this process, the as-prepared PVDF-TrFE solution was placed on the 50 μ m thick Kapton film which has a pre-deposited 20nm gold layer as the bottom electrode. Then, it is spun for 30 seconds at 1000 rpm. The solution can be fully covered on the Kapton substrate. To prevent short-circuiting in the device, after the top electrode was coated, the first layer of spin-coated PVDF was designed to be the solid film, which stayed in an isothermal oven at 60°C for 10min in order to accelerate its solidification process. It is worth to note that even through the pure PVDF-TrFE layer was the solid layer at the beginning of the fabrication process, eventually it became the porous layer because the DMF solvent in the composite solution can dissolve the solid PVDF-TrFE film inevitably. Repeating the whole procedure elaborated above, the layer of PVDF-TrFE/SWCNT was spin-coated on the top of solid PVDF-TrFE film. Following the spin-coating process, the liquid-phase PVDF-TrFE/SWCNT layer was then immediately transferred into the humidity chamber where the relative humidity was maintained at a constant 90% (at 37°C) for more than 4 hours.^{19,20} Throughout this step, the water droplets were able to enter the polymer-rich matrix and form the mesoporous structures in Figure 1(B) and (C). Due to the principle of pore formation in the PVDF-TrFE film, the majority of single-wall carbon nanotubes (SWCNTs) were embedded in the wall of mesoporous structure, but few SWCNT bundles can still be observed shown in Figure 1(D). In Figure S1 (A) in supporting information, some undispersed SWCNT chunks can be observed as well. The bundles of SWCNT were observed with transmission electron microscopy shown in Figure S1 (B). The top electrode was deposited on the surface of mesoporous film after the film was fully dried. The thickness of gold top electrode is 20nm. Finally, the whole film was cut into a number of beam structures, 50mm in length and 5mm in width. In order to further improve the crystallinity of the sample, beams were post-processed by annealing at 135°C for 2 hours and followed by poling.^{21,22} In poling process, the sample was placed in the homemade poling apparatus and applied with about 8kV external electrical voltage at 100°C on a hotplate for 30min. After the samples were cooled down to the room temperature, they were ready for the electrical characterizations.

Here we look into the possibility of employing this energy harvester on a pacemaker lead by using the same level of the mechanical input generated from the deformed lead in dog's heart. We conducted X-Ray image analysis of the lead motion that was provided by our collaborative cardiology team at the University of Texas at San Antonio. The maximum

bending displacement of the lead is in a range between 3mm to 5mm, seen in Figure S2 in supporting information. It is noteworthy that the amount of lead bending displacement and the bending location highly depend on the slack of the lead in heart. In our study, a shaker (modal shop Inc.) sharing the same function of the lead was calibrated to provide a similar level of mechanical displacement input (3mm in this case).

The schematics shown in Figure 2 (A) of the testing strategy involve the change of angle. The beam structure energy harvester was installed on a 3D printed testing platform, and the distance between both ends of the frame was reduced to 80% of the beam's original length. In the first situation, no relative angle formed between two ends of the beam, as shown in Figure 2(A-I). Next, the beam structure energy harvester was examined when the right end of the post was rotated clockwise by 20° and 45° separately, as shown in Figure 2(A-II and III). It is worth mentioning that 45° is the angle boundary of the beam's phase transition from its bi-stability to monostability.²³ As demonstrated in Figure 2 (B) and (C), with angle changing, the three segments of curves obtained from the PVDF-TrFE/SWCNT composite film correspond well with the three testing situations. It obviously reveals the increasing trend with the increment of the angle at the left side of the beam. Specifically, the peak to peak voltage value of the composite film increases from 1.4V to 1.78V, and the current increases from 12.8nA to 17.3nA. In order to provide more evident and meaningful comparisons, the normal mesoporous PVDF-TrFE film was also tested under the same boundary conditions. Results are given in Figure 2(D) and (E). By comparing each column set of results between normal mesoporous film and PVDF-TrFE/SWCNT composite film, it can be seen that both the voltage and current obtained from the PVDF-TrFE/SWCNT composite film are higher than those from the normal mesoporous film. Taking one situation as an example, the voltage and current of the composite film at 45° is respectively ~46 % and ~49% higher than those of the normal film.

From the material point of view, the superiority of the composite film greatly benefits from the application of SWCNT which can serve as the nuclear sites once uniformly distributed in the composite film, thereby enhancing the formation of piezoelectric β -phase of PVDF-TrFE.^{24,25,26} In Figure S3 (A) in supporting information, the enthalpy at the melting point, which is an indication of the crystalline phase (β -phase), was integrated with the melting peak in differential scanning calorimetry (DSC) thermograms. Specifically, the obtained melting enthalpy of normal film and composite film were respectively 15.6 J/g and 23.0 J/g, as shown in Figure S3 (B) in supporting information. With the contribution of SWCNT, the formation of β -phase was enhanced approximately by 47% in the composite film compared with that in the PVDF-TrFE film without SWCNT. The FTIR spectrum in Figure S4 of the supporting information also confirm the enhancement of β phase in the PVDF-TrFE/SWCNT porous composite film due to the presence of SWCNT. Moreover, the SWCNT can act as internal electrodes that can transfer the electrons generated inside the film to the measuring circuit.

According to previous studies,²⁴ the open circuit voltage output, V , for a piezoelectric patch attached to a buckled beam is proportional to the local curvature κ , i.e., $V \propto \kappa$. In the current situation, the PVDF layer is distributed across the whole Kapton film, so in addition to the

local curvature, the output voltage should be proportional to its integration over the beam, i.e.,

$$V \propto \bar{\kappa} = \int_0^L \kappa ds = \int_0^L \frac{d\theta}{ds} ds = \theta_L - \theta_0 \quad (1)$$

where s is the arc length coordinate of the beam, L is its total length, θ_0 and θ_L are the rotation angles at the left and right support of the beam, respectively. According to Eq. (1), the overall curvature can be determined once θ_0 and θ_L is given. To verify the theoretical calculation of $\bar{\kappa}$ and obtain the evolution of local curvature, we construct a finite element (FE) model in Abaqus to simulate the shape evolution of the beam induced by the compression at both its ends and subsequent contact by the shaker. Three rotation angles are exerted at the right support end, as done in our experiment, and the distributions of curvature along the arc length s are given in Figure S5 (A) in supporting information. It can be seen that the rotation of the support end significantly changes the local curvature in the regions $\in [2.5, 5]$, while the curvature in the left region shows small changes for different rotation angles. Such local curvature change causes an increase of overall curvature $\bar{\kappa}$ with the rotation angle (Figure S5 (B)). It can be found that the calculated $\bar{\kappa}$ in the FE analysis is almost equal to the rotation angle θ_L , assigned at the right support end. Because the voltage output is proportional to $\bar{\kappa}$, the case with rotation angle of 45° will correspond to the largest voltage output, which is consistent with the experimental results in Figure 2 (B) and (C).

Fundamentally, the overall electrical outputs generated from the copolymer PVDF-TrFE highly depend on the level of the strain deformation imposed on the dipoles which compose of the fluorine and hydrogen atoms. This inspired us to design an optimized structure that can maximize the overall strain along the beam coupled with the limited displacement from the heart to the piezoelectric polymer in order to generate sufficient energy for charging the pacemaker. Although the electrical output has been improved by adopting the angle rotation scheme at one end of the beam, it is still critical to further explore new strategies to increase the strain deformation of the whole energy harvester and finally improve its power output.

To further improve the energy harvesting performance, a mechanical stop, also be referred to as a mechanical pin, was introduced as an extra boundary condition and imposed on the beam simultaneously with the angle rotation scheme, as shown in Figure 3(A). In order to figure out the best location of the pin such that the beam can generate the highest electrical output, the pin was firstly engaged along the beam transversely; after the voltage profile reached its highest point, the pin was moved perpendicularly until its voltage climbed to the peak point. Here, it is noteworthy that different types of samples, e.g., normal porous film and composite film, have different optimal locations of the mechanical pin. In Figure 3(B) and (C), when both types of boundary conditions were applied, both the voltage and current outputs were significantly improved compared with those from the cases where only angle rotation scheme was implemented. In particular, taking 0° situation as an example, it can be seen that the voltage obtained from composite film increased from 1.4V without pin effect to 2.2V with pin effect, and the current was also improved from 12.9nA to 23.3nA. Next, comparing the results from the normal mesoporous PVDF-TrFE film with those from the

case where neither angle rotation nor mechanical pin effect was adopted, the voltage acquired from composite film who was affected with 45° end-rotation angle and the mechanical pin was improved by approximately 161%, and the current was enhanced by about 200%. From the former works, It has been demonstrated that the electrical output increases with the local curvature of the beam,²⁴²⁵ i.e., a larger degree of bending leads to larger voltage or current output. In our case, the location of mechanical pin plays a role of tuning the curvature of the beam, and thus can be optimized to enhance the output. As shown in the Figure S6, the local curvature at the left support end of the beam with 45° end-rotation angle shows a significant increase with the location of the pin. Comparing the cases with 45° end-rotation in Figure S6 and Figure S5 (A) in supporting information, we can also find a significant increase of local curvature in the area around the tip, which should be the principle reason for the enhanced output for the energy harvester. By far, we have presented and analyzed the comprehensive results of electrical characterizations acquired from the beam-structure energy harvesters composed of either mesoporous PVDF-TrFE film or mesoporous PVDF-TrFE/SWCNT composite film. Here we further evaluate the theoretical power output of the harvesters working in different boundary conditions since this property closely relates to the power requirement of pacemakers in the current medical device market.¹⁴²⁹ Specifically, the instantaneous power output of these two devices was approximately calculated by using equation $P=U^2/R$, where U is the measured voltage and R is the load resistance in SR560.³⁰ As shown in Figure 4, with the influence of the same boundary conditions, the theoretical power output from the beam-structure energy harvester coupled with mesoporous PVDF-TrFE/SWCNT composite film is at least 62% higher than that from the identical structure energy harvester with the regular PVDF-TrFE film. Particularly, when the device with the PVDF-TrFE/SWCNT composite film operates with both the 45° end angle rotation effect and the mechanical pin, the estimated power output is ~7.53 times of that from the device made of pure PVDF-TrFE without the contribution of boundary conditions. From the practical application point of view, power output performance of these devices under different conditions can directly impact their charging period on a pacemaker battery. Based on the power requirement of one pacemaker pulse in the range of 25μJ,²⁹ the charging period of the PVDF-TrFE/CNT energy harvester imposed with 45° end-rotation and the mechanical stop will be about 6 hours. While almost 15.4 hours are needed to charge up the pacemaker to the same power level by using the normal mesoporous PVDF-TrFE film without any boundary conditions. In order to provide a meaningful calculation, the root-mean-square value of power output is used instead of the instantaneous one.

Conclusion

In summary, this work has made two major advances on the design of high-efficacy energy harvesters. On the other hand, with the addition of SWCNT, both the current and the voltage output from the beam-structure energy harvester are improved. For example, in the situation of 0° end rotation angle, the voltage and the current output of the PVDF-TrFE/SWCNT composite film are improved 21.7% and 18.1% respectively, compared with the outputs of the normal mesoporous film. The increase in the crystalline phase in the PVDF-TrFE film due to the presence of SWCNT is proved by the DSC and FTIR. On the other hand, the end-angle rotation and the mechanical pin can be applied in the energy harvesting system to tune

either overall or local curvature of the deformed beam, leading to further enhancement of voltage and current output. To conduct meaningful and evident performance estimations, the theoretical power output of energy harvesters composing mesoporous PVDF-TrFE film or mesoporous PVDF-TrFE/SWCNT composite film under six different boundary condition effects is analyzed, and their charging performance under various situations are also evaluated. The voltage and current of the energy harvester made of composite piezoelectric film under these two boundary conditions were respectively increased by approximately 160.1% and 200.5% compared to the results of its counterpart without imposing any boundary conditions. The estimated power output from the beam structure energy harvester with PVDF-TrFE/SWCNT film increases by 68% to 122% compared with that from the identical structure energy harvester with PVDF-TrFE film corresponding to different boundary condition circumstances. Particularly, the estimated power output of the PVDF-TrFE/SWCNT composite device with a 45° end angle rotation and the mechanical pin is ~7.53 times of that from the device made of pure PVDF-TrFE equipped with no rotational boundary conditions applied. Therefore, our study has paved way for new energy harvesters with higher electrical outputs by utilizing the relatively small mechanical inputs provided by the human body.

Experimental Section

Preparation of PVDF-TrFE with SWCNT solution: In order to prepare 10g 15% PVDF-TrFE with 0.1% wt. single-wall carbon nanotube. Firstly, 10mg SWCNT (from SUNano group) was mixed into 8.5g N,N-Dimethylformamide organic solvent (DMF, purchased from Sigma-Aldrich Inc., US). Then the mixture was handled with a sonication process for about 20mins to ensure that the SWCNT disperses well in the DMF solution.³¹ Secondly, 1.5g PVDF-TrFE powder (Piezotech Inc., France) was blended into the DMF/SWCNT mixture and the whole solution was vigorously stirred under 60°C temperature for at least 4 hours.¹¹ During this period, the PVDF-TrFE power was fully dissolved and the SWCNT can be uniformly distributed into the viscous PVDF-TrFE solution.

Electrical Characterizations: The 3D printed frame was used to accommodate the beam structure energy harvesting unit, meanwhile it can also provide the angle rotation boundary conditions at both ends of the beam. The mechanical pin was placed on the XYZ-direction moveable stage and can be moved along with the beam in order to find the optimized position which can produce the maximized electrical outputs. The whole experimental apparatus is shown in Figure S7 in supporting information. The voltage and the current are measured by using low noise preamplifier (SR 560, Stanford Research Systems) and low noise current preamplifier (SR570, Stanford Research Systems). The self-built LabVIEW program served for data acquisition.

Differential Scanning Calorimetry (DSC): DSC was performed using a Q2000 DSC (TA instrument) with RCS-80 and autosampler. The testing procedure includes a heating process and a cooling process. It started from a heating process that increased the mperature from -40 °C to 200 °C at a heating rate of 10 °C per minute. The sample stayed at 200 °C for 5 minutes, and then the sample was cooled at a rate of 10 °C per minute.

Fourier-transform infrared spectroscopy (FT-IR): FT-IR results were measured by using Jasco 4100 spectro-photometer. Transmittance curve, from 2000 cm⁻¹ to 600 cm⁻¹, was obtained by an integration of 32 scans.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(A) the fabrication process of the mesoporous PVDF-TrFE/SWCNT composite film. The central image is the exploded view of the final beam-structure energy harvester. (B) and (C) the top and cross-section view of the mesoporous PVDF-TrFE/SWCNT composite film, (D) shows the zoomed-in image of the cross-section view showing the presence of the single wall carbon nanotube (with white arrows) inside the film.

Figure 2,
the results of the angle effect on the beam-structure energy harvester. (A) the schematics of testing situations with various angles (0°, 20° and 45°), (B) and (C) the voltage and current output acquired from the mesoporous PVDF-TrFE/SWCNT composite film, respectively, (D) and (E) the comparisons of voltage and current between the normal mesoporous PVDF-TrFE film and the mesoporous PVDF-TrFE/SWCNT composite film, respectively.

Figure 3, the results of both angle effect and mechanical pin effect on the beam-structure energy harvester. (A) the schematics of testing situations with various angles (0°, 20° and 45°) with presence of a mechanical stop, colored green, (B) and (C) the voltage and current output acquired from the mesoporous PVDF-TrFE/SWCNT composite film, respectively, (D) and (E) the comparisons of voltage and current between the normal mesoporous PVDF-TrFE film and the mesoporous PVDF-TrFE/SWCNT composite film, respectively.

Figure 4, the estimation of power performance from the beam structure energy harvester, theoretical power evolution profiles from the beam structure energy harvesters composed of the normal mesoporous PVDF-TrFE film and the mesoporous PVDF-TrFE/SWCNT composite film, separately, associating with 6 different types of boundary conditions.