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Liquid-phase tuning of porous PVDF-TrFE film on flexible substrate for energy harvesting

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Emerging wearable and implantable biomedical energy harvesting devices demand efficient power conversion, flexible structures, and lightweight construction. This paper presents Polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE) micro-porous structures, which can be tuned to specific mechanical flexibilities and optimized for piezoelectric power conversion. Specifically, the water vapor phase separation method was developed to control microstructure formation, pore diameter, porosity, and mechanical flexibility. Furthermore, we investigated the effects of the piezoelectric layer to supporting layer Young’s modulus ratio, through using both analytical calculation and experimentation. Both structure flexibility and stress-induced voltage were considered in the analyses. Specification of electromechanical coupling efficiency, made possible by carefully designed three-dimensional porous structures, was shown to increase the power output by five-fold relative to uncoupled structures. Therefore, flexible PVDF-TrFE films with tunable microstructures, paired with substrates of different rigidities, provide highly efficient designs of compact piezoelectric energy generating devices. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4980130]

Precision healthcare drives the rapid growth of wearable and implantable electronics in the biomedical device industry. Implantable biomedical devices including cochlear implants, pacemakers, cardiovascular defibrillators, and neural stimulators together represent various bioelectronic devices that need long operational lifetime to provide continuous diagnostics and therapy in this mode.1,2 However, providing a long-term power supply to these electronic devices is a critical challenge due to the limited capacity of current batteries in the market.3 In the past decade, various piezoelectric materials have been explored and used for efficient conversion of mechanical energy to electrical energy.4–6 Polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE), a soft and biocompatible material, has demonstrated its applicability in numerous biomedical device energy generators.7,8

We define two sets of requirements for PVDF-TrFE based energy generators for biomedical devices: First, sufficient energy output given limited space for power supply components. Second, mechanical stiffness suitable for wearable and implantable applications. Regarding energy output, PVDF-TrFE nanostructures outperform bulk materials with enhanced piezoelectric effect and higher energy density.9–12

Previous research on energy harvesting optimization mainly focused on resonance frequency analysis in the oscillating range of 100 to 20000 Hz.13,14 Since most mechanical activities in the human body exhibit frequencies of 10 Hz or less, mechanical structure optimization at low frequency becomes an important research direction. Additionally, PVDF-TrFE is assumed to be a flexible device, but bulky membranes will still limit the film’s flexibility and pose as a burden for the wearable and implantable use. For implantable devices, foreign body reactions were significantly enhanced around stiff parts.15 Therefore, a contradiction emerges: energy harvester performance can be improved with increased amount of piezoelectric material, but at a cost to the device’s usability. Using porous structures is one approach to solve the aforementioned problems. However, the use of porous structures in PVDF-TrFE energy harvesters has its challenges. This porous structure requires excellent compressibility, precisely controlled morphology, and mass production technology.

Currently, there are two major methods in porous piezoelectric polymer fabrication: template modeling and phase separation. Template modeling uses nano-scale materials as an additive to the polymer solution. The additive is removed after polymer solidification.16,17 However, this nanomaterial incorporated procedure relies on the substrate material. Therefore, piezoelectric films made by this method are not suitable candidates for mass production over large surface area. Phase separation methods have been previously used to produce porous membranes for filtration, gas-liquid contactors, and battery separators.18–20 Nevertheless, fabrication of high performance phase separation piezoelectric membranes for energy generation remains a challenge as numerous factors influence each other. In order to address this issue, we present a feasible method with repeatable controllability of 3D porous structures to optimize the power output by coupling with substrates of different materials and stiffnesses. We studied the effects of multiple parameters in the procedure of phase separation to tune the pore diameter and porosity. Analytical and experimental results showed a dependence of output voltage on the ratio of Young’s modulus of the piezoelectric film and the substrate. With optimization for both pore diameter variability and mechanical properties, the piezoelectric output can be enhanced by five-fold.

PVDF-TrFE powder (molar ratio: 75/25) was dissolved in a mixture of Dimethylformamide (DMF)-Acetone under magnetic stirring. The volume ration of DMF to Acetone was controlled at 4:0, 2:2, and 1:3. PVDF-TrFE solutions with various concentrations were spin coated on a copper patterned Kapton film (Young’s modulus: 2.7 GPa). Then, the

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film was placed into a chamber with 90% relative humidity at 37 °C and kept for 4 h to allow phase separation between solvent and non-solvent components. After solvent and non-solvent (water) evaporation, a 150 nm thick top copper electrode (3 × 0.5 cm) was deposited onto PVDF-TrFE by E-Beam. The final film thickness was measured with a surface profilometer and found to be approximately 35 μm. Samples were kept in a 120 °C oven for 3 h to increase material crystallinity. The film electrical poling process was performed at 90 °C by applying a 75 V/μm electrical field for 30 min.

The mechanical test was carried out using an Instron material testing system. The PVDF-TrFE piezoelectric coefficient was measured using a Piezotest PM200 piezometer and is listed in Table I. For measuring the Young’s modulus, sample films with the length to width ratio (aspect ratio) of 10 were prepared to avoid the possible clamping effect at the two ends of the film. To measure the piezoelectric performance of the film, the fabricated sample was installed on a motorized test machine. The sample was buckled by the tip of the loading cell. One end of the sample was fixed with a sliding clamp, while the other end of film was periodically contacted the polymer solution, causing the polymer to precipitate due to solvent and non-solvent exchange. The polymer-rich phase forms the porous matrix, while the polymer-poor phase gives rise to the pores. When the film returns to ambient temperature, the condensed water and residual solvent evaporate, leaving behind the 3D polymer scaffold. The temperature, relative humidity, and compositions of solvents are all critical in determining the final film morphology. In this experiment, we controlled the solvent volatility and solution concentration to tune the porosity while maintaining constant humidity and temperature.

Six different solutions with polymer concentrations ranging from 14 wt. % to 26 wt. % were prepared. Fig. S3(a) (supplementary material) shows that the final thickness of the porous film can be controlled with spin speed. In the present investigation, different spin speeds (listed in Table I) were applied to the six solutions in an effort to control the final film thickness to be 35 μm. Pores grew larger as the solvent diffused from the polymer-rich phase to the polymer-poor phase. As shown in Fig. S3(b) (supplementary material), with longer solidification time, pores were allowed to merge with neighboring pores to develop larger. The SEM cross-sectional images of the films with different solvent compositions and polymer concentrations are shown in Fig. 2. The average diameters of pores made from the 14 wt. % and 18 wt. % solutions were 7.30 and 6.65 μm. The pore diameter decreased to 5.80 μm at 22 wt. % and to 4.34 μm at 26 wt. %.

With further increasing polymer concentration, it became more difficult to obtain uniform porous structures by spin coating. Increasing the volatile solvent ratio while maintaining all other parameters also had a significant effect on the final pore diameter. Thus, acetone was introduced, a PVDF-TrFE solvent with a low boiling point, to achieve even smaller diameter than those formed with the 26 wt. % in pure DMF solution. Acetone evaporation led to an increasing local viscosity at the polymer solution-non solvent interface and reduced the formation of large voids. Three 26 wt. % solutions, shown in Figs. 2(a)–2(c), have pore diameters of 3.11 μm, 3.91 μm, and 4.34 μm, respectively. Utilizing these two conditions, the pore diameter can be tuned within the range of 3 μm to 7 μm.

Pore diameters of all film samples were calculated based on the cross sectional SEM. Owing to the characteristics of

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**TABLE I. Summary of experimental conditions and porous film physical properties including pore diameter (D), standard deviation (SD), film porosity (P), Young’s modulus (E), and piezoelectric coefficient (d33).**

<table>
<thead>
<tr>
<th>Concentration (wt. %)</th>
<th>Solvent</th>
<th>V (rpm)</th>
<th>D (μm)</th>
<th>SD</th>
<th>P (%)</th>
<th>E (MPa)</th>
<th>d33 (pC/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>DMF</td>
<td>500</td>
<td>7.30</td>
<td>3.36</td>
<td>83</td>
<td>61</td>
<td>24.1</td>
</tr>
<tr>
<td>18</td>
<td>DMF</td>
<td>900</td>
<td>6.65</td>
<td>2.77</td>
<td>78</td>
<td>100</td>
<td>23.7</td>
</tr>
<tr>
<td>22</td>
<td>DMF</td>
<td>1200</td>
<td>5.80</td>
<td>2.10</td>
<td>71</td>
<td>145</td>
<td>24.4</td>
</tr>
<tr>
<td>26</td>
<td>DMF</td>
<td>1700</td>
<td>4.34</td>
<td>1.41</td>
<td>67</td>
<td>154</td>
<td>25.3</td>
</tr>
<tr>
<td>26</td>
<td>50%DMF, 50%Acetone</td>
<td>2100</td>
<td>3.91</td>
<td>1.02</td>
<td>55</td>
<td>256</td>
<td>24.9</td>
</tr>
<tr>
<td>26</td>
<td>25%DMF, 75%Acetone</td>
<td>2300</td>
<td>3.11</td>
<td>1.04</td>
<td>49</td>
<td>465</td>
<td>25.4</td>
</tr>
<tr>
<td>Solid film</td>
<td>DMF</td>
<td>1000</td>
<td>0</td>
<td>...</td>
<td>0</td>
<td>1530</td>
<td>27.6</td>
</tr>
</tbody>
</table>

---

FIG. 1. Thin film flexible power generator. (a) Schematic of porous film fabrication procedure and (b) unimorph generator structure.
sectioning a porous sample with spherical pores, statistically very few pores can be cut precisely at their diameter, resulting in a pore diameter measurement that is significantly lower than the actual pore diameter of the porous sample—an issue has been largely overlooked by previous researchers.21,22 Thus, we present a quantitative method to accurately quantify randomly distributed pore size characteristics (refer to the supporting material). According to Eq. S10 (supplementary material), the coefficient of variation, defined as the ratio of standard deviation to average diameter, is 28.5%. As listed in Table I, 22 wt. %–26 wt. % samples had pore diameter standard deviations that were close to the calculated numbers, meaning that the pores in the fabricated films are uniform. In the lower concentration samples, uniformity changed as the diameter increased.

The density of the solid PVDF-TrFE films was \( \rho_s = 1874 \, \text{kg/m}^3 \). The density of the porous films prepared from 14 wt. % solution was \( \rho_{pl4} = 319 \, \text{kg/m}^3 \). The low density of the porous films suggests a highly porous structure with a porosity of \( \phi = 83\% \). Density increased with the solution concentration increase to 26 wt. % as well as structure porosity. For 26 wt. % DMF-Acetone (1/3) sample, the porosity dropped to 52.3%.

Films with larger pores and increased porosity exhibited lower Young’s modulus, as shown in Fig. S4 (supplementary material). When film porosity reached 85%, the Young’s modulus dropped from 2 GPa to 3.5 MPa. This result indicated that membrane porosity could be adjusted to reduce Young’s modulus by two orders of magnitude. For implantable and wearable energy harvesters, flexible substrates are desired for a better user comfort and biocompatibility. Polymer coating was applied on a flexible substrate to verify the influence of material coating on the overall structure flexibility. The coated substrate curvature was recorded while a bending moment was applied at one end of the substrate. As shown in Fig. S4(b) (supplementary material), bending stiffness of the solid PVDF-TrFE coated substrate was five times higher than that of the original substrate, while the porous film coated substrate exhibited a relative increase of 82% with the same coating thickness.

The film XRD data of different porosities before and after annealing are shown in Fig. 2. In all annealed samples, the crystallinity is difficult to be directly derived by the XRD intensity,23–25 while the strong diffraction signal should reflect its considerable crystallinity in all annealed samples. FTIR spectra are shown in Figure 3(c), and the polar \( \beta \)-phase bands appear distinctly at peaks in 846, 1285, and 1431 cm\(^{-1}\).26 These vibration bands observed in solid film samples have a higher intensity with respect to the same bands observed in porous film samples. This absorption intensity increase may be caused by an increase in material per volume in the solid film with the same thickness as porous films.

Cantilever structures are commonly used in energy harvesters as a simple beam setup offering high strain with a given applied force. We evaluate the performance of different PVDF-TrFE porosities and Young’s modulus with such structures.27 The piezoelectric charge induced by strain is calculated as

\[
Q = \frac{d_{31} F \eta h_1 h_2 (h_1 + h_2)}{L (c^2 \eta h_1^2 + 4 c^2 \eta h_1 h_2 + 6 c^2 \eta h_2 + 4 c \eta h_1 h_2^2 + 4 c \eta h_1 h_2 + h_2^2)},
\]

where \( h_1 \) and \( h_2 \) are the thicknesses of the PVDF-TrFE film and substrate. \( \eta \) is the ratio of two layers’ Young’s modulus, and \( c \) is the adjusting ratio of the top layer Young’s modulus after electrode deposition. Detailed calculation is included in the supplementary material. The analytical solution of output voltage of the generator, according to its Young’s modulus of different substrates, is shown in Fig. 5. As illustrated in Eq. (1), the output voltage is dependent on applied force, cantilever length, film thickness, and Young’s modulus. For a given substrate material, the key variable in the equation is the modulus ratio \( \eta \), whose effect is the focus of this study.

The variation in PVDF-TrFE Young’s modulus could influence strain and position of the neutral axis. Previous research largely focused on a combination of piezoelectric materials with rigid cantilever structures in which the piezoelectric material’s Young’s modulus needs to be closer to the substrate’s mechanical property.28,29 In such a case,
decreasing Young’s modulus will serve little purpose. As a requirement of flexible harvesters for implantable applications, the structure stiffness of the harvester should be orders of magnitude lower than that of previous devices. This means that a lower Young’s modulus of the piezoelectric film is desired.

To verify the influence of variable film porosity on enhancing the output power via Young’s modulus control, two Kapton films (2.7 GPa) with 50 μm and 5 μm thicknesses were used as substrates. The thick film was used as a conventional substrate for piezoelectric generators while the thin film was used as a flexible device suitable for implantable and wearable applications. Each kind of Kapton film was mounted with seven films of different porosities prepared from solution conditions in Table I. For the deformation of the generator, the bending machine was employed with a 0.5 N periodic bending force along the poling direction at the edge of cantilever. A charge amplifier was used to measure the charge output directly, so the effect of the variable dielectric constant of the porous material can be avoided.

The voltage output of the solid PVDF-TrFE film with both substrates was found to be under 3 V as shown in Fig. 4(a). The solid PVDF-TrFE film had the highest Young’s modulus and highest output on the rigid substrate. On the flexible substrate, the measured voltage increased as the film porosity increased and the Young’s modulus decreased. As a comparing group, the 6 μm solid PVDF-TrFE film was prepared with the same condition. On the rigid substrate, the 6 μm film showed a 0.7 V output lower than the 35 μm film. On the flexible substrate, the output of the 6 μm film was 3.1 V, higher than 35 μm, but lower than other porous films. In Fig. 4(b), the 26% DMF-Acetone (1/3) film’s voltage output showed a different trend on the two substrates. It dropped from 2.6 V to 2 V on the rigid substrate, as compared with the solid PVDF-TrFE film. However, on the flexible substrate, the output performance increased to 3.1 V, higher than the performance of the solid PVDF-TrFE film in Fig. 4(a). As mentioned above, the thinner and more flexible substrate makes the neutral line move towards the PVDF-TrFE layer surface, and it causes the generator to receive more tensile or...
compressive stress during stretching and pressing. As shown in Figs. 4(c) and 4(d), the 22% and 14% PVDF-TrFE-DMF samples exhibit an enhanced voltage output with the porous structure on the flexible substrate. This conclusion also agrees with the analytical result in Fig. 5 which showed a peak in the low Young’s modulus range. Therefore, the flexible substrate with porous film coating significantly increased the output power of the generator.

The analytical solution and full experimental results were shown as blue lines and red squares in Fig. 5. In Fig. 5(a), with a rigid Kapton substrate, the output monotonically decays as the Young’s modulus reduces. The solid PVDF-TrFE film, with 1.5 GPa modulus, has the highest output. This is because on the rigid substrate, the neutral axis is located closer to the PVDF-TrFE surface as the Young’s modulus decreases, which results in lower potential differences between the top and bottom electrodes. As a comparing group, the 6 µm solid PVDF-TrFE film was prepared with the same condition. On the rigid substrate, the 6 µm film showed a 0.7 V output lower than the 35 µm film. On the flexible substrate, the output of the 6 µm film was 3.1 V, higher than 35 µm, but lower than other porous films. In Fig. 5(b), a thinner Kapton substrate, with a much less rigid substrate, and conventional solid PVDF-TrFE film exhibit output far from the optimized peak around 48 MPa Young’s modulus. With the lowest Young’s modulus PVDF-TrFE films (14% DMF), the output with the flexible substrate was five times higher than with the rigid substrate. Trends in analytical and measured data demonstrated a strong validation of the piezoelectric effect in flexible beam structures. Therefore, it is evident that by controlling the porous structure, there is the ability to tune the film’s mechanical flexibility that best works with different substrates.

Combining theoretical and experimental studies, we determined the optimal Young’s modulus ratios for maximum voltage and energy outputs of PVDF films. For flexible substrates suitable for implantable applications, the optimized output from porous coating is five-fold higher than that from non-controlled samples. These results suggest that utilizing porous PVDF-TrFE material fabrication and Young’s modulus optimization theory, with light weight and flexible construction mechanical, makes aforementioned films a prime candidate for implantable biomedical device development.

See supplementary material for calibration of pore diameter, calculation of cantilever beam, photograph of mechanical test setup, pore diameter controlling parameters, and film mechanical properties tests.

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