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Electrostrictive Polymers for Mechanical-to-Electrical Energy Harvesting

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Contents

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Abstract:

Research of electrostrictive polymers has generated new opportunities for harvesting energy from the surrounding environment and converting it into usable electrical energy. Piezoelectric ceramic based devices have long been used in energy harvesting for converting mechanical motion to electrical energy. Nevertheless, those materials tend to be unsuitable for low-frequency mechanical excitations such as human movement. Since organic polymers are typically softer and more flexible, the translated electrical energy output is considerably higher under the same mechanical force. Currently, investigations in using electroactive polymers for energy harvesting, and mechanical-to-electrical energy conversion, are beginning to show potential for this application. In this paper we discuss methods of energy harvesting using membrane structures and various methods used to convert it into usable energy. Since polymers are typically used in capacitive energy harvesting designs, the uses of polymer materials with large relative permittivities have demonstrated success for mechanical to electrical energy conversion. Further investigations will be used to identify suitable micro-electro mechanical systems (MEMs) structures given specific types of low-frequency mechanical excitations (10-100Hz).

SECTION I. Introduction

Natural energy sources are attracting a rising amount of interest due to increasing environmental concerns. Electroactive polymer (EAP) research is one of the new opportunities for harvesting energy from the natural environment and converting it into usable electrical energy. Piezoelectric ceramics, such as lead zirconate titanate (PZT), materials used for mechanical-to-electrical energy harvesting tend to be unsuitable for low-frequency mechanical excitations such as human movement. Polymer materials are typically more flexible, allowing the electrical energy output to be considerably higher under the same mechanical energy input. Several applications have been identified where free, unused mechanical energy could be used to generate electrical energy and are summarized in Table I.

There are various methods to convert mechanical energy from vibrating or moving objects into electrical energy. Electroactive polymers possess semi-crystalline structures in which the centers of positive and negative charges do not overlap, yielding dipoles. When subjected to mechanical vibrations, mechanical strain is applied to these materials and leads to distortion of the dipoles, creating electrical charge. The electrical energy can be harvested by storing it in capacitors or rechargeable batteries.[1]

Table I Frequency and acceleration of various vibration sources[1]

Vibration source	Frequency (Hz)	Acceleration amplitude (m/s^2)
Car instrument panel	13	3
Casing of kitchen blender	121	6.4
Clothes dryer	121	3.5
HVAC vents in office building	60	0.2-1.5
Car engine compartment	200	12
Refrigerator	240	0.1
Human walking	2-3	2-3

The following electroactive polymers have demonstrated piezoelectric, pyroelectric or ferroelectric properties: Nylon-11,[2] polylactic acid (PLLA),[3] poly(lactic-co-glycolic acid) (PLGA),[4] and poly(vinylidene fluoride) (PVDF).1 PVDF and its copolymers have demonstrated the best all-around electroactive properties.[5,1] Many of the interesting properties of PVDF, in particular those related with its use as a sensor or actuator, are related to the strong electrical dipole moment of the PVDF which results from the electronegativity of fluorine atoms as compared to those of hydrogen and carbon atoms.[5,6] In this way, each chain possesses a dipole moment perpendicular to the polymer chain. This semicrystalline polymer shows a complex structure and can present several distinct crystalline phases related to different chain conformations. As shown in Fig. 1, the β-phase possesses the highest dipole moment per unit cell when compared to the other two phases (α & λ) and is therefore the most responsive piezoelectric polymer.

Previous processes used to manufacture PVDFs piezoelectric β-phase have been limited to drawn films. Therefore in order to obtain the electroactive phases of PVDF, different strategies have focused on the inclusion of specific copolymers such as Poly(vinylidene fluoride-Trifluoroethylene), P(VDF-TrFE).[6–7,8,5] As shown in Fig. 2, P(VDF-TrFE) always exhibits the ferroelectric β crystalline phase.[1,5] The fluorine atom from TrFE stabilizes the β-crystalline phase and discourages α-crystalline phase formation.[1] This property permits P(VDF-TrFE) copolymer to be produced in the form of thin-films by spin coating, and allows a suitable control of sample thickness which is ideal for the production of energy harvesting microstructures.

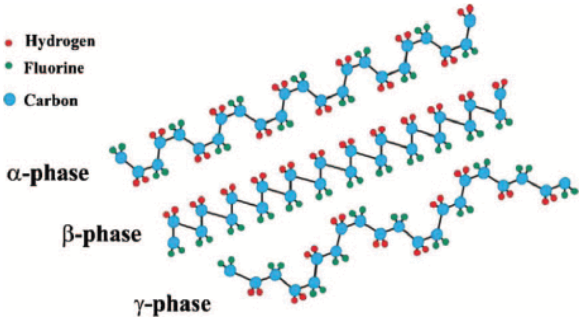

Fig. 1. Schematic representation of the chain conformation for the α,β, and λ phases of PVDF[5]

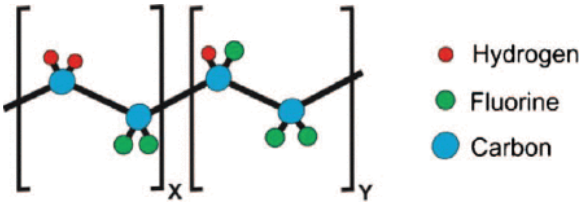

Fig. 2. Schematic representation of the P(VDF-TrFE) repeat units[5]

SECTION II. Methodology

In the case of energy harvesting using an EAP such as P(VDF-TrFE), the vibration or mechanical energy sources either have low motion frequencies or low acceleration. A thin and flat form factor allows the EAP element to readily react to the motion of the host structure. Therefore, cantilever geometry is one

of the most used structures in piezoelectric energy harvesters, especially for mechanical energy harvesting from vibrations[1,9,10] (Fig. 3).

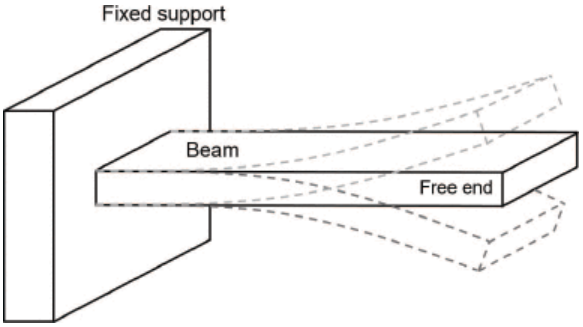

Fig. 3. Cantilever beam with rectangular cross section under free vibration

Harvester performance can be optimized to specific applications provided a known resonant frequency from Fig. 4, which is given by: $w_{nf} = {a_n}^2\sqrt{\frac{EI}{mL^4}}$ where $\alpha_n = 1.875, 4.694, 7.885$.[11] Therefore the resonance frequency of a simply supported cantilever beam can be calculated using (1) where E is the Young's modulus, I is the moment of inertia, L is the length of the cantilever, w is the width of the cantilever, m is the mass per unit length of the cantilever beam, and $\alpha_n = 1.875$ is the eigenvalue for the fundamental vibration mode.[1]

$$f_r = \frac{{\alpha_n}^2}{2\pi}\frac{1}{L^2}\sqrt{\frac{EI}{mw}} \tag{1}$$

$$f_r = \frac{{\alpha'_n}^2}{2\pi}\frac{1}{L^2}\sqrt{\frac{K}{m_e + \Delta mK}} \tag{2}$$

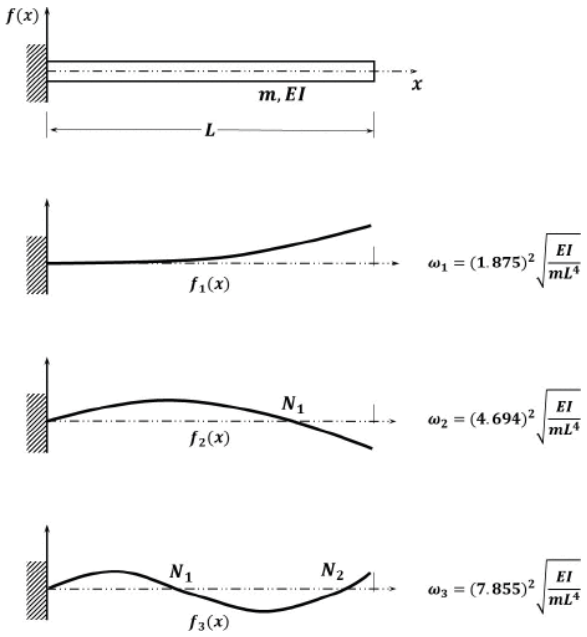

Fig. 4. The first three undamped natural frequencies and mode shapes of a cantilever beam

In order to further lower the resonance frequency of the cantilever microstructure, a proof mass can be attached to the free end of the cantilever (Fig. 5). In which case (1) can be approximated by (2), to include the proof mass Δm where $\alpha_n'^2 = \alpha_n\ ^2\sqrt{0.236/3}, m_e = 0.236mwL$ is the effective mass of the cantilever, and K is the effective spring constant of the cantilever.[1,12]

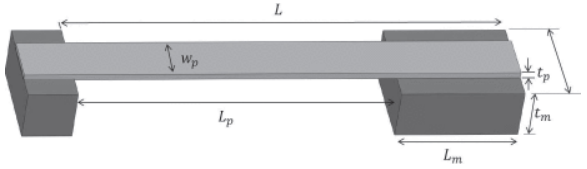

Fig. 5. Proof mass attached to the free end of a cantilever beam

SECTION III. Designs and Fabrication

Fig. 6 shows a large bimorph structure that will be used to experimentally validate the aforementioned design rules. Energy harvester performance can be predicted based on the dimensions, mass of the cantilevers, and proof mass. In this structure, a thin layer of P(VDF-TrFE) will be deposited and patterned into a cantilever and bonded with a top and bottom electrodes (positive and negative) serving as conductors of the generated charge. Fig. 7 shows the post processing steps for PolyMUMPs energy harvesting structures using P(VDF-TrFE) EAP. Once processed, the P(VDF-TrFE) has to be poled in order to obtain piezoelectricity. Temperature and electric field poling conditions are critical to the resulting piezoelectricity of the ferroelectric polymer.[13,14] Two widely used methods are electrode poling and corona poling. The first method involves the poling electric field being applied through two metal electrodes. The second, corona poling, is a method in which a high electric field is applied directly to the polymer film without metal electrodes. Electrode poling is the safest and easiest to conduct. However, corona poling is more efficient because of the reduced risk of localized electric breakdown occurring, in which case the corona poling process would not be affected.[14]

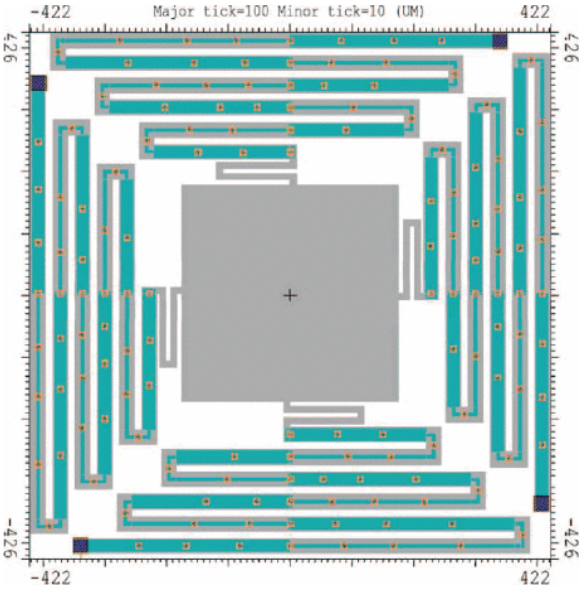

Fig. 6. PolyMUMPs design for a bimorph structure with large center proof mass for energy harvesting. Overall dimensions are $1mm \times 1mm$

SECTION IV. Results and Discussion

Since polymers are typically used in capacitive energy harvesting designs, the use of polymer materials with large relative permittivity have demonstrated the most success for mechanical to electrical energy conversion.[1,16] The characteristic equations of piezoelectric materials are $D_3 = \varepsilon_{33}E_3 + d_{31}T_1$ and $S_1 = d_{31}E_3 + s_{11}T_1$, where D_3 is the electric displacement in the polarization direction, S_1 is the strain in the axial direction, ε_{33} is the dielectric permittivity of the piezoelectric material in the polarization direction at constant stress condition, E_3 is the electric field in the polarization direction, T_1 is the stress in the axial direction of the cantilever, d_{31} is the piezoelectric coefficient, and s_{11} is the compliance of piezoelectric material under constant electric field condition.[17,18] Given the area of the piezoelectric layer (AP), the generated piezoelectric charge can be calculated as:

$$\int^{AP} D_3 dA = d_{31}S_1/s_{11} + \epsilon_{33}^{-}E_3 dA \tag{3}$$

where: $\varepsilon_{33}^{-} = \varepsilon_{33}(1 - k_{31}^2)$ and $k_{31}^2/(\varepsilon_{33}s_{11})$[17]

Table II Properties for selected piezoelectric ceramics (PZT) and PVDF[15]

	PZT-5H (ceramic)	PVDF (polymer)
Density (g/cm^3)	7.65	1.78
Dielectric constant ε_r	3250	6.0
Young's modulus Y_33 (GPa)	71.4	2
Mechanical qualtiy factor Q_m	32	10
Piezoelectric charge constant d33 (pC/N)	590	25
Piezoelectric charge constant d31 (pC/N)	-270	12-23
Electro-mechanical coupling factor k33	0.75	0.22

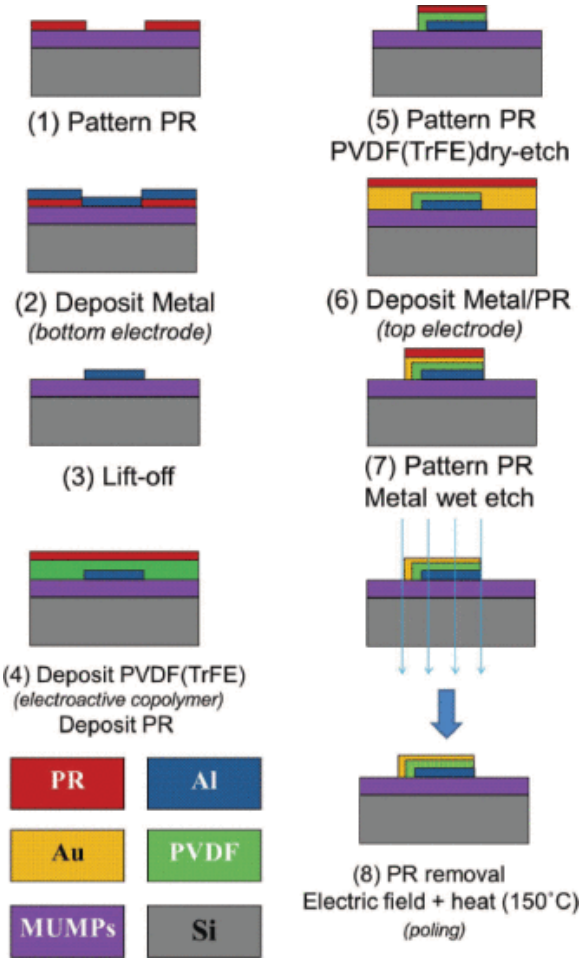

Fig. 7. PolyMUMPs post-processing fabrication steps involving the deposition and patterning of PVDF films

A key factor in determining the field-effect mobility of a EAP device is the specific processing steps involved in the deposition and annealing of the P(VDF-TrFE) due to the resulting orientation and porosity of polymer grain boundaries.[19] Typically, spin coating is the technique used to deposit P(VDF-TrFE), however it has also been shown that electrophoretic deposition (EPD) can be used to deposit PVDF thin films (≤1μm) in a more conformal manner.[20]

Electrophoretic deposition (EPD) is an electrodeposition technique in which films are formed by charged particles migrating under the effect of high electric fields. These charged particles are generated in the regions where polymer is dissolved in an acetone solution. A proven process has been demonstrated by way of electrophoretic deposition for 2.5 minutes and $170\mu A/cm^2$ constant current density $(130 - 190V)$ after which the film is annealed with a resulting $\sim 0.5\mu m$ thick film. Ultimately EPD films tend to be more conformal than spin coat films due to their higher unannealed density.

A model representing a bimorph energy harvesting structure was designed in simulation taking into account the additional deposition steps involved. Finite element modeling was conducted using CoventorWare© to evaluate the addition of PVDF and top gold electrode deposition (post PolyMUMPS processing). More specifically, partial bimorph cantilever beam material properties and geometries were

evaluated. In modeling and simulation, the addition of PVDF and gold reduced the deflection by approximately 66% independent of actuator length (Table III).

Table III Results of cantelever deflection with/without post processing

Length	Deflection $(2\mu m)$ $(Poly2, Au)$	Deflection $(3.5\mu m)$ $(Poly2, Au, PV\,DF, Au)$
$500\mu m\rightarrow$	$24\mu m$	$8.2\mu m$
$625\mu m\rightarrow$	$37\mu m$	$13\mu m$
$750\mu m\rightarrow$	$54\mu m$	$18\mu m$
$875\mu m\rightarrow$	$73\mu m$	$25\mu m$
$1000\mu m\rightarrow$	$95\mu m$	$32\mu m$

SECTION V. Conclusion

A mechanical analysis of an experimental bimorph structure was provided and led to key design rules for postprocessing steps to control the performance of the energy harvester. In this work, methods of materials processing and the mechanical to electrical conversion of vibrational energy into usable energy were investigated. Materials such as P(VDF-TrFE) were evaluated and presented a large relative permittivity and greater piezoelectric β-phase without stretching. The next step is to fabricate a suitable polymer based energy harvesting device and perform measurements of the fabricated samples. Results will be used to validate the proposed mathematical model relating key features of a unique cantilever geometry. Future work will also consist of fabrication process refinement to more precisely control harvester performance characteristics.

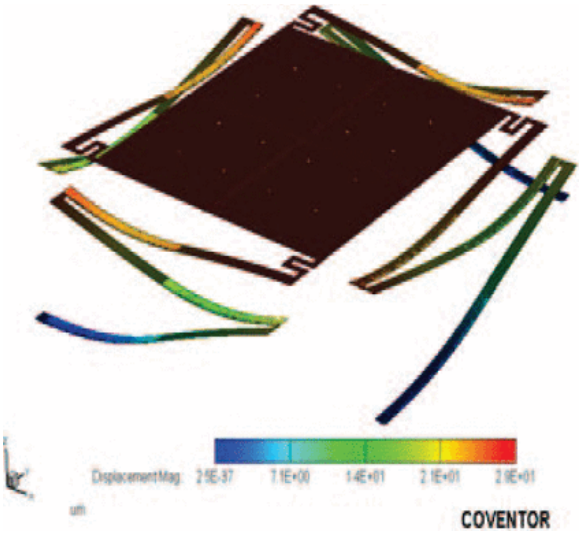

Fig. 8. MEMS large aperture actuator assembly mechanical analysis

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References

1. H. Li, C. Tian, Z. D. Deng, "Energy harvesting from low frequency applications using piezoelectric materials", *Applied Physics Reviews*, vol. 1, no. 4, pp. 0-20, 2014.

2. S. C. Mathur, J. I. Scheinbeim, B. A. Newman, "Piezoelectric properties and ferroelectric hysteresis effects in uniaxially stretched nylon-11 films", *Journal of Applied Physics*, vol. 56, no. 9, pp. 2419-2425, 1984.

3. L. Huang, X. Zhuang, J. Hu, L. Lang, P. Zhang, Y. Wang, X. Chen, Y. Wei, X. Jing, "Synthesis of Biodegradable and Electroactive Multiblock Polylactide and Aniline Pentamer Copolymer for Tissue Engineering Applications", *Biomacromolecules*, vol. 9, no. 3, pp. 850-858, mar 2008.

4. D. J. Bryan, J. B. Tang, S. A. Doherty, D. D. Hile, D. J. Trantolo, D. L. Wise, I. C. Summerhayes, "Enhanced peripheral nerve regeneration through a poled bioresorbable poly(lactic-co-glycolic acid) guidance channel", *Journal of Neural Engineering*, vol. 1, no. 2, pp. 91, 2004.

5. P. Martins, A. C. Lopes, S. Lanceros-Mendez, "Electroactive phases of poly(vinylidene fluoride): Determination processing and applications", *Progress in Polymer Science*, vol. 39, no. 4, pp. 683-706, 2014.

6. Y. G. Jiang, S. Shiono, H. Hamada, T. Fujita, D. Y. Zhang, K. Maenaka, "Reactive ion etching of poly(vinylidene fluoride-trifluoroethylene) copolymer for flexible piezoelectric devices", *Chinese ScienceBulletin*, vol. 58, no. 17, pp. 2091-2094, 2013.

7. F. Bauer, E. Fousson, Q. M. Zhang, L. M. Lee, "Ferroelectric copolymers and terpolymers for electrostrictors: Synthesis and properties", *IEEE Transactions on Dielectrics and Electrical Insulation*, vol. 11, no. 2, pp. 293-298, 2004.

8. H. Han, Y. Nakagawa, Y. Takai, K. Kikuchi, S. Tsuchitani, Y. Kosimoto, " Microstructure fabrication on a \$beta\$ -phase PVDF film by wet and dry etching technology ", *Journal of Micromechanics and Microengineering*, vol. 22, no. 8, pp. 085030, 2012.

9. S. Saadon, O. Sidek, "Micro-Electro-Mechanical System (MEMS)-Based Piezoelectric Energy Harvester for Ambient Vibrations", *Procedia - Social and Behavioral Sciences*, vol. 195, pp. 2353-2362, 2015.

10. S. Boisseau, G. Despesse, B. A. Seddik, "Electrostatic Conversion for Vibration Energy Harvesting", *Small-Scale Energy Harvesting*, pp. 1-39, October 2012.

11. Y. Liu, T. Nabatame, T. Matsukawa, K. Endo, S. O'uchi, J. Tsukada, H. Yamauchi, Y. Ishikawa, W. Mizubayashi, Y. Morita, S. Migita, H. Ota, T. Chikyow, M. Masahara, "Comparative Study of Charge Trapping Type SOI-FinFET Flash Memories with Different Blocking Layer Materials", *Journal of Low Power Electronics and Applications*, vol. 4, no. 2, pp. 153-167, 2014.

12. A. S. Y. Ho, J. S., Poon, "Energy transfer for implantable electronics in the electromagnetic midfield (invited paper)", *Progress In Electromagnetics Research*, vol. 148, pp. 151-158, August 2014.

13. M. Wegener, R. Gerhard-Multhaupt, "Poling of piezoelectric polymer cables and assessment of their sensor properties", *Proceedings. 11th International Symposium on Electrets*, no. 1, pp. 379-382, 2002.

14. F. A. Costache, C. Schirrmann, R. Seifert, K. Bornhorst, B. Pawlik, H. G. Despang, A. Heinig, "Polymer energy harvester for powering wireless communication systems", *Procedia Engineering*, vol. 120, pp. 333-336, April 2016.

15. N. K. Jha, D. Chen, *Nanoelectronic circuit design*, 2011.

16. A. Plihon, V. Fischer, F. D. D. Santos, R. Gwoziecki, "Printed actuators made with electroactive polymers on flexible substrates", *9th IEEE International Conference on Nano/Micro Engineered and Molecular Systems IEEE-NEMS 2014*, pp. 68-71, 2014.

17. L. Zhang, S. R. Oh, T. C. Wong, C. Y. Tan, K. Yao, "Piezoelectric polymer multilayer on flexible substrate for energy harvesting", *IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control*, vol. 60, no. 9, pp. 2013-2020, 2013.

18. "LT 0915 REC C", L. Technology, *Typical application*, pp. 1-42, 2013.

19. S. Film, T. Oh, *Organic Thin-Film Transistors Using*, vol. 5, no. 1, pp. 23-29, 2006.

20. J. D. Foster, R. M. White, *ELECTROPHORETIC DEPOSITION OF THE PIEZOELECTRIC POLYMER P (VDF-TrFE)*, pp. 30.