

Songklanakarin J. Sci. Technol. 35 (5), 605-610, Sep. - Oct. 2013



Original Article

Experimental assessment of polyvinyledene fluoride coupled through standard approach for vibration-energy harvesting

Prissana Rakbamrung^{1*} and Nantakan Muensit^{2,3}

¹ Faculty of Education, Suratthani Rajabhat University, Mueang, Surat Thani, 84000 Thailand.

² Department of Physics, Faculty of Science,

³Center of Excellence in Nanotechnology for Energy (CENE), Prince of Songkla University, Hat Yai, Songkhla, 90112 Thailand.

Received 18 May 2012; Accepted 12 July 2013

Abstract

This work presented the experimental analysis which focused on the realization of active volume within a crystalline phase of semi-crystalline PVDF samples on energy harvesting efficiency. The transformation of mechanical into electrical energy was performed by PVDF connected directly in series to a standard interface circuit. This work investigated both commercial and synthesized PVDF. The maximum power of 2.6 mW was measured across the matching load of 1 M Ω at 70 Hz exciting frequency from commercial PVDF of 28 mm thickness. A decrease in power was observed when the sample thickness increased. Generated power of prepared- and commercial-PVDF, however, were almost the same for the thickness of about 50 mm with an active area of 4 cm².

Keywords: energy harvesting, poly(vinylidene fluoride), standard approach

1. Introduction

Energy harvesting has received quite a lot of attention and grows at a rapid pace. Transformation of ambient energy into a conveniently used form like electrical energy is an exciting and rapidly developing area of research. The use of large-scale energy sources such a solar and wind is progressively increasing. A large percentage of recent research is directed to the other end of the scale, capturing small-scale ambient energy (vibration and heat), which is useful for low power electronic devices. Especially, harvesting vibration energy has recently been given much attention due to an inexpensive maintenance process and a cheaper way for capturing enormous energy losses in industrial processes and

* Corresponding author. Email address: prisana_sru@hotmail.co.th technologies (Glynne-Jones *et al.*, 2001; Ng and Liao, 2005; Liu *et al.*, 2007). Several methods by which electrical energy can be obtained from such a source include piezoelectric, electromagnetic, and electrostatic generators (Roundy *et al.*, 2002; Glynne-Jones *et al.*, 2004; Mitcheson *et al.*, 2004). Piezoelectric materials are widely available because of their excellent electromechanical properties and they do not require an external voltage source.

The strong piezoelectricity of polyvinylidene fluoride or PVDF, was observed by Kawai (1969), and the ferroelectricity in the PVDF was found two years later. Among the electroactive polymers, the PVDF is semi-crystalline and has superior mechanical characteristics. A semi-crystalline PVDF was polymerized for the first time in the 1940s. It has a simple chemical structure $(-CH_2-CF_2-)_n$, lied between polyethylene (PE) $-(CH_2-CH_2)_n$ and polytetrafluoroethylene (PTFE) $-(CF_2$ $-CF_2)_n$. Common phases of PVDF are α -, β -, γ - and δ -phase. The two most common phases are the helical α -phase with a transgauche (TGTG) molecular conformation resulting in an antipolar unit cell, and the β -phase with an all-trans (TT) conformation resulting in a polar unit cell whose dipole moments (μ) aligned perpendicular to the chain axis (Lovinger, 1983). The β -phase shows the highest piezoelectric effect of the four crystal phases, but in actual PVDF sample there are likely many crystal phases coexisting. The dipole moment of β -PVDF is aligned in the same direction leading to the highest dipole moment $(7.0 \times 10^{-30} \text{ Cm} \text{ monomer}^{-1})$ (Zhu *et al.*, 2008). Unlike β -PVDF, the dipole moment of α crystallites is oriented in opposite directions resulting in a zero net polarization. In order to enhance the piezoelectric properties of PVDF especially increasing the piezoelectric coefficient of PVDF of about 20 pC·N⁻¹ (Davis, 1978), the stretching and poling process is the most common approach. Therefore, the present work aims to study the use of poled PVDF for converting low-frequency vibration into usable electrical energy by using a standard approach in order to increase the potential in commercial sectors of PVDF.

2. Methodology

2.1 Preparation of the poled PVDF

PVDF samples in this work were synthesized as described earlier by the authors (Rakbamrung and Muensit, 2010). The neat PVDF is a non-polar α -phase; to enhance such polar structures it was stretched to its final dimension without rupture. The stretched sample was electroded by sputtering an aluminum layer and subsequently subjected to a DC electric field of 40 MV·m⁻¹ in a silicone-oil bath at 80°C for 2 hrs to increase the β -phase. Then it was a poled PVDF (Muensit *et al.*, 2011).

2.2 Sample characterization

Xray diffractometer (Philips X'pert X-ray diffraction system) was used to distinguish the phases of the sample. The monomers and phases that existed in the PVDF were precisely determined by a Fourier Transform Infra-Red (FTIR) spectra recorded in the range of 500-4,000 cm⁻¹ (Perkin-Elmer, EQUINOX 55, Bruker, with KBr as blank). All samples including their morphology and infra-structure were visualized by using atomic force microscopic (AFM) technique (Nanosurf, Switzerland). The sample was then heated from room temperature (25°C) to 250°C with a heating rate of 10°C min⁻¹ to perform a thermal analysis by using a differential scanning calorimetry (DSC) apparatus (Perkin Elmer). Its melting temperature, T_m and enthalpy could be determined at the onset of the thermal peaks and from the peak areas, respectively. The percentage of the molecules in the crystalline phase (crystallinity) was calculated from the heat of fusion of the sample to that of a 100%-crystalline PVDF (i.e., 104.7 J \cdot g⁻¹). The fraction of β -phase was calculated according to Greorio and Cestari (1994). Dielectric constant, ε_{1} and dielectric loss (tan δ) were measured by a HP-4263B LCR

Meter.

2.3 Experimental set-up

The driving cantilever beam is using an electromagnet connected to a function generator, which applies an electromagnetic force on the magnetic tip mass. The benefit in placing the mass at the tip of the beam is to reduce the resonances of the vibrating structure. A photonic sensor (MTI-2100, MTI Instrument, Inc) was used in order to monitor the displacement (Figure 1). This sensor is also connected to an oscilloscope (TDS 420 A Trektronix) for detecting the minimum and maximum values of the displacement. In addition to the switching interface, the harvesting stage is composed of a full diode bridge rectifier (W04M) and a smoothing capacitor (C_s) of 1 µF. This interface is connected to a resistance box, whose value can be made to vary in order to determine the power generation abilities of the device with respect to the load R₁.

Each sample was bonded on a spring steel cantilever beam with a rectangular cross-section whose dimensions are $55 \times 17 \times 0.5$ mm, and featuring a magnetic tip mass of 1.645 g. The physical properties of the beam were given in Table 1. Assuming the weak coupling system, the output power *P*, which was equivalent to the power dissipated by the load *R*, was calculated from Equation 1.

$$P = \frac{V_{DC}^2}{R} \tag{1}$$

where V_{DC} is the rectified voltage.



Figure 1. Energy harvesting structure: (a) schematic and (b) a pictorial view.

Table 1. Steel beam characteristics.

Physical properties	Value
Young's modulus (Y)	210 GPa
Poisson's ratio (v)	0.3
Density (p)	7.5

3. Result and Discussion

Micropatterns of neat PVDF and poled PVDF show peaks at about 18.5°, 26.8° and 39° corresponding to (020), (021), and (100) reflection, which clearly revealed the presence of α -phase PVDF (Figure 2.), while the peak corresponded to (110, 200) at 20° refers to orthorhombic β -phase. The relatively high beta phase was observed from the pole PVDF. Some properties for prepared PVDF in comparison to those of the commercial piezoelectric are shown in Table 2. An increase in melting point (T_m) of PVDF with stretched and poled suggested that its crystals are thicker than another as supported by the result of its crystallinity. The results can be ascribed as the effect of the relatively high temperature and applied mechanical force, which lead to the closely packed polymer chain intern to the formation of βphase. The higher packing polymer chain and higher melting temperature as occurred in β -phase is because of the conformation of all transplanar zigzags in its structure. FTIR spectra of α - and β -phase can be observed in all samples. The FT-IR spectrum ascribed the C=C (874, 1,683 cm⁻¹), C-H (835, 1,400 cm⁻¹), and C-F (762, 1167, 1,230 cm⁻¹) stretching vibrations. The transmittance band in the wave number of about 762, 798, 874 and 1,230 cm⁻¹ was clearly characteristic for the non polar TGTG conformation, the so called α -phase of PVDF. The required β -phase as a major phase appeared in the PVDF after stretched and poled. The vibration band, which correspond to the β -phase are described by CF₂ bending and CH₂ rocking. The piezoelectric voltage constant (g), the piezoelectric charge constant (d) and Figure of merit (FOM) which affected the output electric power were not much

different for a commercial and poled PVDF at a thickness of about 50 $\mu m.$

Using the AFM approach with non-contact mode provides a 3D profile of the surface on a microscale and using a feedback loop to monitor changes in the amplitude due to attractive van der Waals forces the surface topography can be measured. In Figure 3, the neat surface of the PVDF sample has a root-mean-square roughness of 15 nm (Figure 3a). It was 10 nm in the stretched one (Figure 3b) and further reduced to be 8 nm after the poling process (Figure 3c). The darkened area in the figure corresponds to the antiparallel orientated molecular regions, which were lesser and smaller in the poled sample, indicating the transformation from α to β phase which correspond to the results in XED analysis. However, the images were not clearly displayed in the poling domain due to the low resolution of this method.

Piezoelectric characteristics were summarized in Table 3. The harvested power depends on active area of PVDF (Figure 4) so that the higher (dipole) area as a results in greater in charge generated by PVDF. Typically, an increase in piezoelectric layer thickness resulted in the piezoelectric rigidity. However, the obtained piezoelectric rigidity is much small compared to that of the beam. Therefore, the beam bending remains almost constant and independent from the piezoelectric



Figure 2. XRD patterns for neat PVDF and stretched and poled PVDF.

	Commercial PVDF	Neat PVDF	Poled PVDF
Dimension	$1 \text{ cm} \times 4 \text{ cm} \times 52 \text{ mm}$	$1 \text{ cm} \times 4 \text{ cm} \times 50 \text{ mm}$	$1 \text{ cm} \times 4 \text{ cm} \times 50 \text{ mm}$
Density (g/cm^3)	1.6	1.8	1.8
T_{m} (°C)	171.5	159.0	160.8
Crystallinity (%)	52.8	57.3	51.6
FTIR data	In-plane bending or rocking	CF ₂ -bending, CH ₂ -rocking	In-plan bending
	(745 cm^{-1}) referred to β -phase	(745 cm^{-1}) referred to β -phase	referred to α-phase
β -phase (%)	45.24	-	42.70
ε_r , tan $\delta(1 \text{ kHz})$	12, 0.01	5,0.02	9,0.02
Coupling factor	-	-	0.0293
$d_{33} (pm/V)g_{33} (m^2/C)$	62.140.59	-	59.200.74
$d_{33} \bullet g_{33} (GJ/m^3)$	27.5	-	22.73

Table 2. Properties of prepared PVDF (this study) compared to commercial ones from Measurement Specialties, Inc..



Figure 3. AFM images of the surfaces for (a) neat- (b) stretched- and (c) stretched and poled-PVDF.

Table 3. Piezoelectric characteristics.

	Value			
Parameter	Commercial PVDF		Poled PVDF	
	28 µm	52 µm	50 µm	100 µm
Blocking capacitance, $C_0(nF)$	1.83	0.68	0.52	0.37
Displacement, u (mm)	64.64 1.11	65.58 1.09	1.08	69.10 1.07

layer thickness. For the experiment, an increase in thickness of the PVDF insert led to a decrease in output power of about 1-2 μ W (as seen in the Figure 5). This related to the decline in blocking capacitance (C_o) from 1.8 to 0.4 nF. Also, the bending displacement of the beam decreased of about 10-40 μ m as the piezoelectric layer increased. This phenomenon may be because the deformation of the beam is not linear; the effect of each small piece of the beam is different when the beam is vibrating, which lead to a decline of PVDF deformation and as a results a lower charge was generated. The charge/voltage generations of the PVDF samples are shown in Table 4. The maximum harvested power of 2.6, 1.4, and 1.7 μ W at 1.5 V were obtained from using a 28 μ m commercial, 50 μ m poled, and 52 μ m commercial PVDF element, respectively.

4. Conclusion

This work indicates that the piezoelectric activity in the PVDF material seems to depend upon the active area within the crystalline phase of the polymer. The 50 μ m poled PVDF could harvest energy from vibration and change it into



Figure 4. Experimental harvested power as a function of resistive load for 28 mm-commercial PVDF at different active area.

useful electrical power with a value of an order of 1.4μ W for the matching load of $1.6 M\Omega$ at a relatively low operating frequency. These polymers can thus be utilized as energy resources such as rechargeable lithium battery (Roundy *et al.*, 2003).

V_{DC(max)} $P_{(max)} \ (\mu W)$ Sample Type Sample I (max) thickness (µm) (V) (μA) Commercial PVDF 28 2.0 2.6 1.3 52 1.7 1.7 1.0 Pole PVDF 50 0.9 1.6 1.4 100 1.1 0.9 0.8





Figure 5. Harvested power as a function of resistive load for all the PVDF samples of the dimension of 1x4 cm.

Acknowledgment

The authors would like to thank the Prince of Songkla University, HatYai, and Suratthani Rajabhat University, Surat Thani, both Thailand, for support.

References

- Davis, G.T., Mckinney, J.E., Broadhurst, M.E. and Roth, S.C. 1978. Electric field induced phase changes in poly (vinylidene fluoride). Journal of Applied Physics. 49, 4998.
- Greorio, R. Jr. and Cestari, M. 1994. Effect of crystallization temperature on the crystalline phase content and morphology of poly(vinylidene fluoride). Journal of Polymer Science Part B: Polymer Physics. 32, 859-870.
- Glynne-Jones, P., Tudor, M.J, Beeby, S. P. and White N.M. 2004. An electromagnetic, vibration powered generator for intelligent sensor systems. Sensors and Actuators A. 110, 344-349.
- Glynne-Jones, P., Beeby, S.P., and White, N.M. 2001. Towards a piezoelectric vibrationpowered microgenerator. Science, Measurement and Technology, Institute of Electrical and Electronic Engineers Proceedings. 148, 68-72.
- Kawai, H. 1969. The Piezoelectricity of Polyvinylidene Fluoride. Japan Journal of Applied Physics. 8, 975-976.

- Liu, W.Q., Feng, Z.H., He, J. and Liu, R.B. 2007. Maximum mechanical energy harvesting strategy for a piezoelement. Smart Materials and Structures. 16, 2130-2136. doi:10.1088/0964-1726/16/6/015.
- Lovinger, A.J. 1983. Ferroelectric Polymer. Science. 220, 1115-1121.
- Mitcheson, P., Miao, P., Start, B., Yeatman, E., Holmes, A. and Green, T. 2004. MEMS electrostatic micro-power generator for low frequency operation. Sensors and Actuators A. 115, 523-529.
- Muensit, N., Thainiramit, P. and Rakbamrung, P. 2011. Mechanical-to-Electrical Energy Harvested with Polyvinylidene Fluoride. Proceedings of the 6th Annual Conference of the Thai Physics Society SPC011, Pattaya, Chonburi, Thailand. March 23-26, 2011, 258-259.
- Ng, T.H. and Liao, W.H., 2005. Sensitivity analysis and energy harvesting for a selfpowered piezoelectric sensor. Journal of Intelligent Material Systems and Structures. 16, 785-797.
- Rakbamrung, P. and Muensit, N. 2010. Low- and high-loaded electroactive polyvinylidene fluoride polymers. Journal of Materials Science and Engineering. 4, 23-31.
- Roundy, S.J. 2003. Energy scavenging for wireless sensor nodes with a focus on vibration to electricity conversion, Ph.D. Thesis, Faculty of Engineering, University of California, 2003.
- Roundy, S., Wright, P.K., and Rabaey, J. 2002. Micro-electrostatic vibration-to-electricity converters Proceedings of the American Society for Mechanical Engineering 2002 International Mechanical Engineering Congress and Exposition.
- Roundy, S., Wright, P.K. and Rabaey, J. 2003. Computer Communications. 26, 1131–1144.
- Zhu, G.D., Zeng, Z.G., Zhang, L. and Yan, X.J. 2008. Piezoelectricity in β-phase PVDF crystals: A molecular simulation study. Computational Materials Science. 44, 224-229.
- Zhu, M., Worthington, E. and Njunguna, J. 2009. Institute of Electrical and Electronic Engineers Transactions on ultrasonics, ferroelectrics, and frequency control, 56, 1309.

List of abbreviations

Antiresonant frequency	f
Atomic force microscopic	
Blocking capacitance	C_{θ}
Density	ρ
Dielectric constant	εŗ
Dielectric loss	tanδ
Differential scanning calorimetry	DSC
Dipole moments	μ
Displacement	и
Figure of merit	FOM
Load resistance	R_{L}
Melting point	T_m
Output power	$P^{\tilde{m}}$
Piezoelectric charge constant	d
Piezoelectric voltage constant	g
Poisson's ratio	v
Polyvinylidene fluoride	PVDF
Rectified voltage	V_{DC}
Resonant frequency	\tilde{f}_r
Smoothing capacitor	\dot{C}_s
Young's modulus	Ÿ