

Design and Characterization of Piezoelectric P(VDF-TrFE) Thick Film on Flexible Substrate for Energy Harvesting

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Abstract— This paper discusses on the design and fabrication steps of piezopolymer using poly(vinylidene fluoride) trifluoroethylene, P(VDF-TrFE) thick film on the flexible substrate using screen-printed method. Polyethylene terephthalate, PET film was used as a substrate to hold P(VDF-TrFE) thick film in between sandwiched layers of electrode-piezopolymer-electrode. The P(VDF-TrFE) thick film is then annealed at 100 °C and polarized at 100 V for the film and inspected under EDS, FESEM and XRD for the characterization process. The flexible piezoelectric P(VDF-TrFE) thick film is able to generate maximum output peak power of 4.36 μW at an external load of 1kΩ with generated maximum peak-to-peak voltage about 3.0 V for energy harvesting applications when using impact force test from free-fall drop plasticine of 0.2 N was applied to the thick film.

Index Terms– Energy Harvesting; Flexible Piezoelectric; P(Vdf-Trfe); Screen Printing.

I. INTRODUCTION

Energy harvesting is defined as conversion of ambient energy from the surrounding energy sources such as sunlight, temperature differences and vibration for on-demand energy application whenever it is needed. Nowadays with recent advances application such as self-power wireless and MEMS technology, energy harvesting system is an alternative solution of the conventional battery. Most of the low power electronics and wireless sensor use batteries as their main power sources, but the life span of the batteries is short and limited as compared with working life of the devices. Therefore, many researchers have been conducted energy harvesting system applications as self-power devices or wireless sensor application. In this paper, the energy harvesting is limited to micro energy harvesting which can be generated from μW to mW of level power where the micro energy harvesting sources is based on mechanical vibration, mechanical stress and strain only [1].

Piezoelectric material can have an electrical field induced inside its boundaries when mechanical stress is applied on its piezoelectric material such as quartz, rochelle salt, barium titanate. The first piezoelectric effect was discovered by Jaques and Pierri Curie in 1880 [2]. Piezoelectricity effects are catergorised into direct effect and indirect effect. The direct effect cause voltage generated when tensile stress

applied on the piezoelectric material. The indirect effect is the deformation of the piezoelectric material when external electric field is applied. The direct and indirect piezoelectric effects have many applications as the effects of conversion electrical energy into mechanical energy and vice versa. The applications include pressure sensor, energy harvester, actuator, and ultrasonic waves application. The couple of electromechanical of piezoelectric materials can be modeled by two linearized equations [3].

Direct piezoelectric effect:

$$D_i = e_{ij}^{\sigma} E_j + d_{im}^d \sigma_m \quad (1)$$

Indirect piezoelectric effect

$$\varepsilon_k = d_{jk}^c E_j + S_{km}^E \sigma_m \quad (2)$$

where: D_i = Dielectric displacement

ε_k = Strain vector

E_j = Electric field vector

σ_m = Stress vector

d_{im}^d = Piezoelectric constants

d_{jk}^c = Piezoelectric coefficients

e_{ij}^{σ} = dielectric permittivity

S_{km}^E = elastic compliance matrix

The superscripts d and c refer to the direct and indirect effects, respectively, and the superscript E and σ indicate that the quantity is measured at constant electric field and constant, stress respectively.

Piezoelectric materials can be classified into piezopolymers and piezoceramics. Piezoceramics have large electro-mechanical coupling constants and provide high energy conversion rate, but they are too brittle to use general shape energy transducer. On the other hand, piezopolymers have smaller electromechanical coupling constants compared to the piezoceramics, but they are very flexible. Other advantages of piezopolymers are they can be cured at lower temperature and can be formed any flexible shapes as compared to piezoceramics [4-6].

In 1969, Kawai discovered the polymer of polyvinylidene fluoride (PVDF) exhibit a strong piezoelectric effect for energy harvesting application [7]. PVDF is a semi-crystalline material which it has some crystalline phase regions surrounded by amorphous regions. PVDF has four main crystalline phases: α , β , γ and δ . PVDF is a semi-crystalline material which it has some crystalline phase regions surrounded by amorphous regions. PVDF has four main crystalline phases: α , β , γ and δ . The relative quantity of each is dependent on the thermal, mechanical and electrical processing conditions used to produce the PVDF film. The most general form is non-polar α -phase which does not have any piezoelectric properties. Only highly oriented β -phase is responsible for the piezo- and pyroelectric properties of the polymer [8]. It was shown that α -phase can be converted to β by subjection to mechanical stretching. As an enhanced PVDF, PVDF copolymer - poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) with addition of TrFE into the PVDF system plays an important role in the phase transition behavior. This is because of the size of the additional fluorine atom, the copolymer will crystallize directly in β -phase. Therefore, no mechanical stretching is required during the process of polling, and this copolymer can be directly used to produce final structures from the solution of P(VDF-TrFE) [9].

The output of energy harvesting can be calculated in open circuit with respect to the relationship between voltage generated and external resistor load. The formula can be derived as:

$$P = \frac{V^2}{R_L} \quad (3)$$

where: P = Power (watt, W)
 V = Voltage generated by piezoelectric material (volts, V)
 R = Resistor load (resistance, Ω)

This work reports design and fabrication steps of piezopolymer using P(VDF-TrFE) material on flexible substrate (Melinex 723) by screen printing method. In order to investigate the characteristic of the proposed energy harvesting system, EDS, FESEM and XRD are carried out and then free-drop test are conducted to validate the performance of the proposed energy harvesting system.

II. DEVICE DESIGN AND FABRICATION

Piezopolymer P(VDF-TrFE) is fabricated using screen printed method and Figure 1 shows a schematic diagram of the sandwiched thick film with its dimension of the harvester and electrode layers are shown in Table 1. The sandwiched cantilever structure consists of four layers which are flexible substrate, top and bottom electrode layers and piezopolymer P(VDF-TrFE) layer.

Table 1
 Dimension of fabricated harvester

Layer Name	Parameter, $L \times W$ (mm)
P(VDF-TRFE) layer	2.5 x 2.0
Top Electrode	3.4 x 1.0
Bottom Electrode	3.4 x 0.8

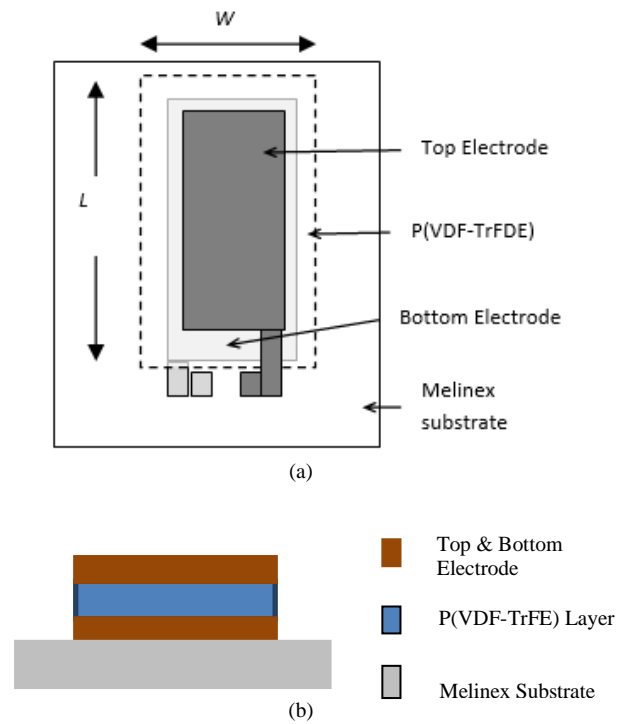


Figure 1: (a) Plan view and (b) side view of the schematic diagram of the sandwiched thick film.

III. MATERIAL SELECTION

A. Substrate Material

We have decided polyethylene terephthalate (PET: Melinex) polyester film substrate, supplied by Dupont Teijin Films, since this is the best predominant substrate for flexible electronic industry. This substrate is good resistance of temperature up to 260°C [10]. Furthermore, this substrate offers excellent handling properties such as good adhesion to UV printing inks and screen inks for both sides film.

B. Conductive material

Leed-Ink silver conductive polymer paste (DT1201) have been chosen for both electrodes (top and bottom) since its good bonding conductor with adaptable PET substrate were identified. This conductive paste can be cured 130°C to 30 min which its lower than melting temperature of piezopolymer P(VDF-TrFE) layer [11].

C. Piezopolymer material

In order to achieve a materials with flexible structure and low curing temperature, we used a high piezopolymer coefficient and low curing temperature (about 100°C) of poly(vinylidene fluoride-trifluoroethylene) or P(VDF-TrFE) with a molecular weight of 350,000 $gmol^{-1}$ or [75:25mol%] manufactured by Kureha, Japan [12].

IV. EXPERIMENTAL DETAILS

A. Fabrication of P(VDF-TrFE) thick film

For the thick film fabrication, P(VDF-TrFE) (75:25mol %) powder were disintegrated with N,N-dimethylformamide (DMF, 99.8 vol%, Sigma-Aldrich), in concentration of 15wt%. Then, the powder was dissolved in DMF by magnetic stirring and ultrasonic bath for 20 min to ensure that the solution was fully dissolved. Details of the P(VDF-TrFE) dispersions parameters are shown in Table 2.

Table 2
List of P(VDF-TrFE) dispersions and parameters

Parameter of P(VDF-TrFE)	Solvent	Stirring Temperature (°C)	Stirring Time (hr)
Layer 1	DMF	100 °C	1
Layer 2	DMF	24-26°C	4
Layer 3	DMF	24-26°C	4

In the next step, the bottom silver polymer electrode layer was screen-printed using screen stencil onto blank Melinex PET substrate. After printing of bottom electrode, the substrate was cured at 130°C using oven for 30 min. Then, it was used to deposit P(VDF-TrFE) thick film to an approximation of thickness, 18µm thick by using screen printing method on a flexible PET substrate (Melinex) with thickness of 75 µm. In order to increase the thickness of P(VDF-TrFE) layers for the optimum output. The experiment printing of P(VDF-TrFE) layers are printed via casting method with thickness of 60 µm and 100µm thick film.

Before deposition of top electrode layer, the P(VDF-TrFE) thick film was dried with temperature 80°C for 2 hr in order to remove the residual solvent. The P(VDF-TrFE) thick film was subsequently annealed in an ambient environment oven at 100°C for 1/2 hour to obtain a smooth and crystalline surface with reduced porosity [13].

Final layer was the top electrode layer where it was screen-printed with similar method as bottom electrode layer. Table 3 show the summary of paste properties and printed layer process parameters. The P(VDF-TrFE) thick film was successful fabricated as shown in Figure 2 using screen-printed method.

Table 3
Summary of paste properties and printed layer process parameters.

Layer/Parameter Name	Material	Printing Method	Curing Condition
Top and bottom electrodes	Silver polymer paste	Print screen	Oven 130°C, 30min
Layer 1	Poly(vinylidene fluoride trifluoroethylene)	Print screen	Oven 80°C, 2hr
Layer 2 & 3		Casting	Hot plate annealing 100°C, ½ hr

Electrical poling was performed across the thick films using D.C. power supply at 100 V for 20 min at 100°C (near to the Curie temperature of P(VDF-TrFE)). This polarization is to align the domain dipole according to the polarity of the DC voltage.

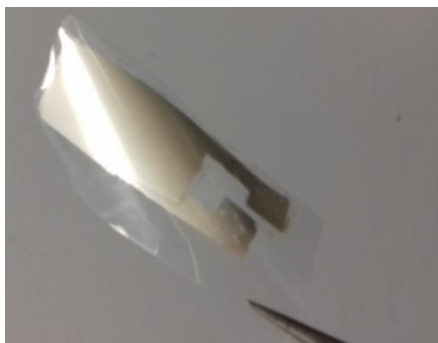


Figure 2: Fabricated P(VDF-TrFE) thick film device

B. Microstructure inspection and characterization

In Figure 3, it is confirmed that P(VDF-TrFE) and palladium silver electrode and silver polymer electrode paste are successfully printed on the Melinex substrate. Figure 3 (a) shown EDX spectrum of P(VDF-TrFE) films with nominal heterogeneities. The elemental composition composed of F, C, Ag, and Pd elements using silver palladium electrode while silver polymer electrode paste are consists of elemental composition of C, Ag, O, Cl, and Si as shown in figure 3(b).

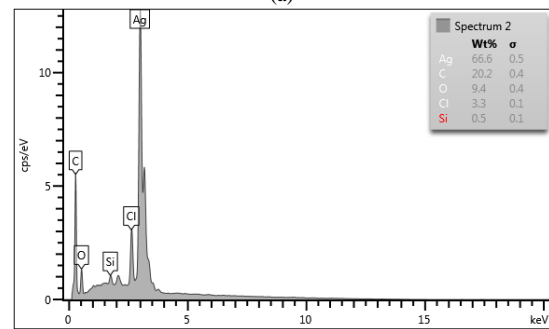
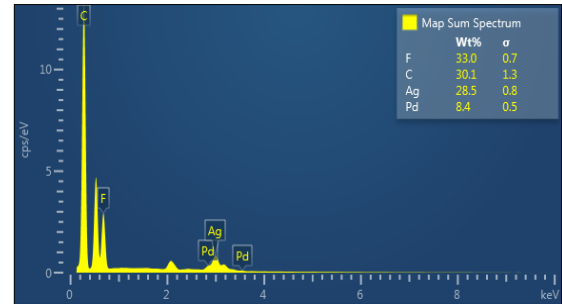
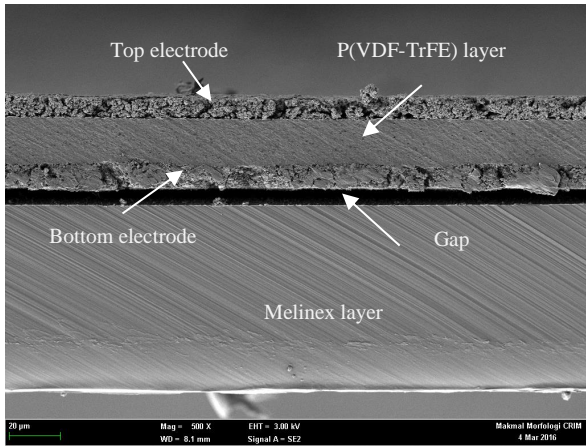


Figure 3: EDX spectrums for P(VDF-TrFE) film (a) silver-palladium electrode and (b) silver polymer electrode.

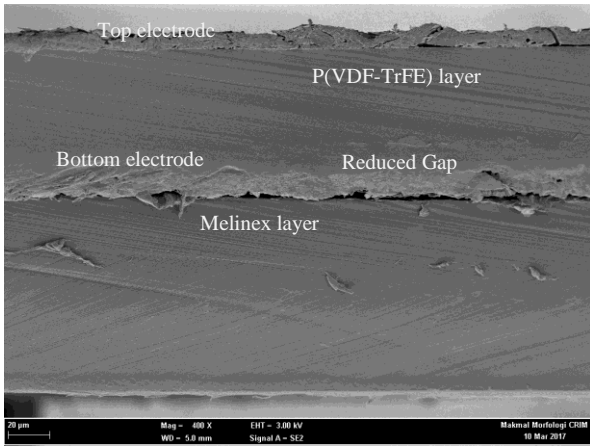
Figure 4 shows the cross-sectional morphology of printed P(VDF-TrFE) thick film was measured and checked by using FESEM after completing the printing process and the results are shown in Table 4. Figure 4 (a) shows the presence of a gap of 6.5 µm before and after the hot plate annealing due to the weak bonding deposition of palladium silver conductor paste in bottom electrode with Melinex® substrate. We have managed to reduce the gap issue using silver polymer paste where it can be reduced about 3.3 µm and the bonding deposition of silver electrode paste with Melinex substrate as shown in Figure 4(b).

The quality of printed PVDF layers on Melinex substrate can be examined by using optical microscopy to determine crystallinity in the PVDF layers [14]. Figure 5 (a) shows the surface microstructure of the annealed P(VDF-TrFE) thick films that we observed using FESEM at accelerating voltage 3kV with 2K and 20K magnification. It was found that an improvement of crystallinity with 4hr of stirring time with DMF compared with 1hr of stirring time with DMF (Figure 5b). In thick film technology, crystallinity plays important during the fabrication process which it affected the output of performance film [15]. As a solution to improve the crystallinity of P(VDF-TrFE) is longer stirring time of P(VDF-TrFE) with DMF during the fabrication process. Figure 6 shown the intensity peak of P(VDF-TrFE) increased ten times in 4 hours stirring as compared with an hour of stirring in DMF solution. Therefore, parameter of

layer 2 and layer 3 were chosen instead of parameter of layer 1 for the entire experimental setup. The diffraction peak in the XRD patterns with β -PVDF, appeared at $2\theta = 20.03^\circ$ assigned to (110/200) reflection planes [16-18].



(a)

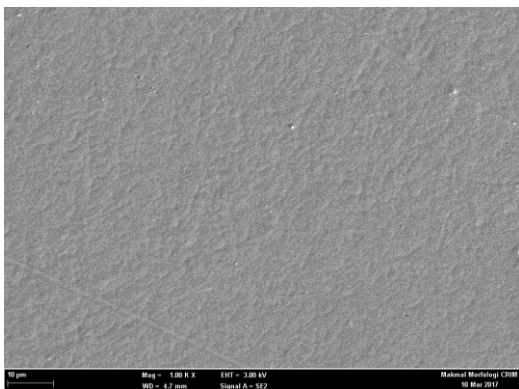


(b)

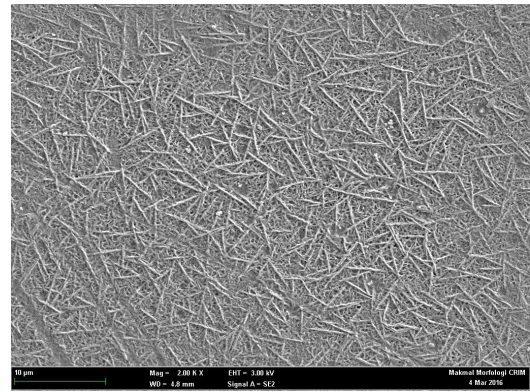
Figure 4: Cross section FESEM images of P(VDF-TrFE) film (a) silver metal based electrode and (b) silver polymer based electrode.

Table 4
Measured layer thicknesses

Layer name / μm	Bottom electrode	P(VDF-TrFE)	Top electrode
Silver palladium	10.50	-	9.38
Silver polymer	9.78	-	9.78
Layer 1		17.64	
Layer 2		60.08	
Layer 3		98.24	



(a)



(b)

Figure 5: FESEM images of P(VDF-TrFE) film annealed at 100°C with (a) 4 hr stirring and (b) 1 hr stirring.

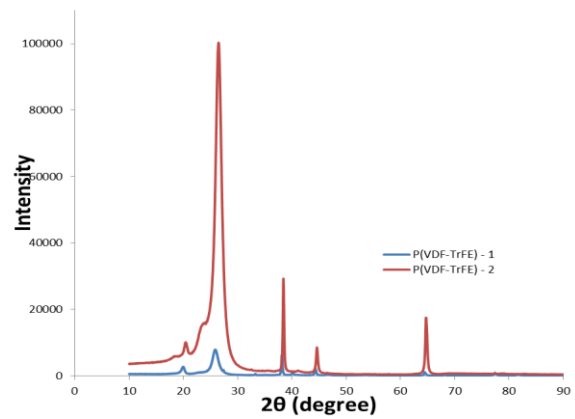


Figure 6: X-ray diffraction patterns P(VDF-TrFE) thick film (a) 4 hr stirring and (b) 1 hr stirring.

C. Electrical Properties

To obtain piezoelectric charge coefficient, d_{33} of fabricated P(VDF-TrFE) thick film using direct measurement (Berlincourt method). Figure 7 shown a commercial Berlincourt piezometer (Model ZJ-6B Quasi-Static Piezo d_{33} d_{31} Meter, Institute of Acoustics Chinese Academy of Sciences) and we managed to measure piezoelectric charge coefficient, d_{33} , about 13 pC/N^{-1} which it is as good as BaTiO_3 thick film piezoelectric application [19].



Figure 7: Direct measurement of piezoelectric coefficient, d_{33} .

D. Experimental Setup

Figure 8 shows the instantaneous AC voltage generated from P(VDF-TRFE) material under impact force test during

the experiment, which was captured using digital oscilloscope. The experimental setup was carried out using free-fall drop impact test on the fabricated energy harvester by dropping a known mass of plasticine with varying weights from 0.03 N to 1N (refrains from falling out of the target by using a plastic cylinder as shown in figure 9) at a fixed height of 20cm.

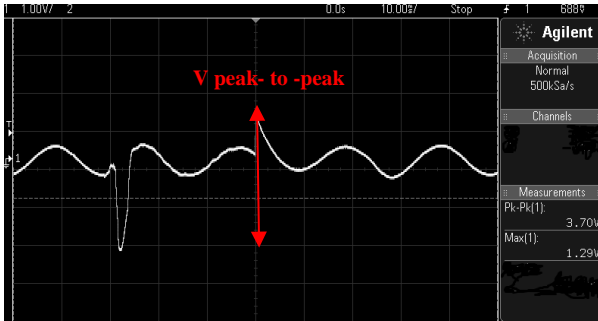


Figure 8: Instantaneous output AC voltage peak-to-peak of P(VDF-TrFE) material tested under impact force .

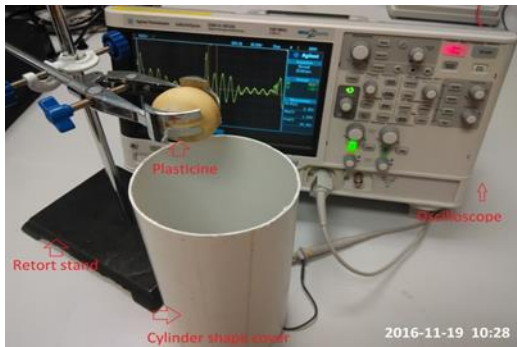


Figure 9: Free-fall drop impact test.

V. RESULT AND DISCUSSION

The optimum thickness layers of P(VDF-TrFE) is the 100 μ m (layer 3) compared with other thickness layers of 18 μ m (layer 1) and 60 μ m (layer 2). Figure 10 shows layer 3 generated highest voltage output about 3.06V at 0.2N load is applied on the P(VDF-TrFE) layer. When the force exceeding 0.7 N, the average output voltage settled down to 2.70V for all thickness of layers.

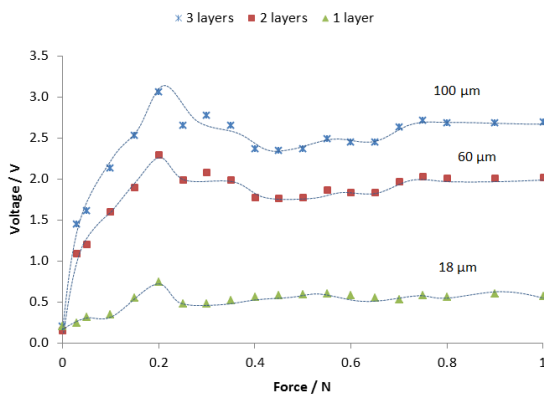


Figure 10: Voltage output vs force.

The fabricated device was connected to external resistive load varied from 700 Ω to 5 k Ω for measuring electrical output power whenever an impact force is applied on the P(VDF-TrFE) layer. Figure 11 shows layer 3 is best

maximum output peak power of 4.36 μ W is being measured across an optimum external load of 1k Ω when fixed load at 0.2N.

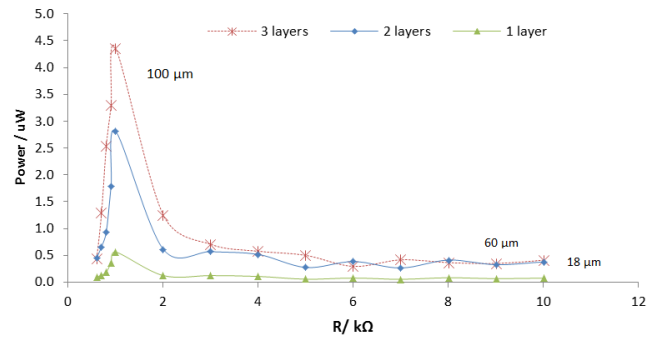


Figure 11: Power vs resistive load.

VI. CONCLUSION

Piezoelectric P(VDF-TrFE) thick films were successfully fabricated using screen-printed method and characterized on Melinex substrate as an energy harvester. The consistent experimental result of the performance shows layer 3 of P(VDF-TrFE) [thickness of 100 μ m] is the best thickness for maximum output peak power of 4.36 μ W at an external load of 1k Ω with generated maximum peak-to-peak voltage about 3.0V and piezoelectric charge coefficient, d33 of 13 pC/N⁻¹. Further research is in progress to develop an enhanced structure for higher and efficient performance thick film of polymer piezoelectric in micro-energy harvesting systems.

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