An improved method for piezoelectric characterization of polymers for energy harvesting applications

E Gusarova, B Gusarov, D Zakharov, M Bousquet, B Viala, O Cugat, J Delamare and L Gimeno

1 G2Elab, Univ. Grenoble Alpes, F38000, Grenoble, France
2 CNRS, Univ. Grenoble Alpes, F38000, Grenoble, France
3 CEA, LETI, MINATEC Campus, F38000, Grenoble, France

E-mail: boris.gusarov@g2elab.grenoble-inp.fr

Abstract. This work presents an improved method for measuring the direct piezoelectric voltage and energy of flexible polymers. Well-controlled stress is applied with a four-point bending system and voltage is measured in real open-circuit conditions. The presented method separates the piezoelectric part from the measurement part by introducing a mechanical switch, allowing instantaneous post-deformation discharge measurements. Oscilloscope and contact-less electrostatic voltmeter are compared. Direct piezoelectric measurements under open-circuit conditions have been performed on commercial PVDF (polyvinylidene fluoride) and its copolymers. Significant differences to data sheet values (close-circuit conditions) are reported and commented.

1. Introduction

Conventional direct piezoelectric characterization can be hampered by large electrical losses and uncontrolled charge leakage into the circuit during measurements. This may result in lower detected voltage and possible underestimation of the material properties. Taking into account the low permittivity or capacitance of polymers compared to piezoelectric ceramics, this problem becomes even more important to solve for flexible organic piezoelectric films.

Usually, direct piezoelectric response measurements for polymers are made with a standard oscilloscope with closed-circuit connection [1, 2], or by using sophisticated charge-amplifier circuits [3, 4]. Here we propose a simple and accurate method for measuring the voltage after mechanical deformation of flexible organic films with real open-circuit conditions, virtually with no charge leakage. For this purpose, we introduce a mechanical switch into the measurement circuit to separate the piezoelectric part (generator) from the measuring part (collector). Two technics using oscilloscope and contact-less electrostatic voltmeter are compared. Results for commercial PVDF and copolymer of P(VDF-TrFE) are reported and compared to data sheet values (measured in closed-circuit conditions).
2. Experimental
2.1. Experimental set-up
The proposed method for measuring the voltage output introduces into the circuit a mechanical switch, which separates charges generation from charges collection for voltage measurement. The switch is kept open during the mechanical deformation of the polymer while space charges are produced. When the deformation is completed, the switch is closed and space charges are converted to free charges at the electrodes, and transferred at once into the measurement circuit.

The output voltage is measured with two technics: first using a standard oscilloscope (for this work Agilent Technologies DSO1014A was used) and second with a non-contact electrostatic voltmeter (in this work a TREK 370 voltmeter). The latter measures the electrostatic sample surface potential without physical contact, making the impedance of such system virtually infinite, thus eliminating potential residual charge leakage that could take place at the oscilloscope load input.

A schematic representation of the circuit is shown on figure 1.

![Schematic presentation of the measurement circuit with a switch, an oscilloscope and a contact-less electrostatic voltmeter.](image)

Figure 1. Schematic presentation of the measurement circuit with a switch, an oscilloscope and a contact-less electrostatic voltmeter.

This real open-circuit set-up allows ideal space charges generation when applying stress to the polymer material. For the purpose of applying stress, we use a controlled high precision four-points bending system. Once the charges are generated and the switch is closed (A), the discharge takes place over few tens milliseconds (B) as shown in figure 2. The corresponding electrical energy can be calculated from time dependent voltage by equation (3) with integration limits from A (start of discharge) to B (discharge completed).

\[ E = \frac{1}{R} \int_{A}^{B} V^2 dt \]  

(1)

As can be seen from figure 2, both methods lead to identical remarkable high voltage output range of the order of hundred volts (here with commercial PVDF at 0.5% strain). This is considerably higher than that of the conventional oscilloscope measurement which reduces to the order of ten volts (see dotted line in figure 2).

When comparing real open-circuit measurement results with the oscilloscope and the electrostatic voltmeter, one see a difference in the time-dependence of charges decay, as it greatly depends on the load resistance (10 MΩ was used for oscilloscope and 1 MΩ for electrostatic voltmeter). However, the calculated energy remains resistance-independent. During this work most of the piezoelectric measurements were performed with the switch and oscilloscope set-up with a load resistance of 10 MΩ.
Figure 2. Typical discharge curves of PVDF after 0.5% deformation measured with oscilloscope and electrostatic voltmeter. For both cases the switch is closed at time zero. The curve with oscilloscope was made with 10 MΩ, and the curve with electrostatic voltmeter was made with 1 MΩ resistance to demonstrate the impact of resistance on discharge behavior. A conventional closed-circuit measurement with an oscilloscope (R=10 MΩ) is shown in dash for comparison.

Table 1. Properties of a commercial PVDF sample used in present work [5, 6, 7].

| Name             | Length(mm) | Width(mm) | Thick(mm) | $d_{31}$ ($\mu$m/V) | $g_{31}$ (V m/N) | $k_{31}$ (%) | YM (GPa) |
|------------------|------------|-----------|-----------|--------------------|------------------|--------------|----------|
| LDT1             | 30         | 12.19     | 0.028     | 23                 | 0.216            | 12           | 2-4      |
| PVDF             | 20         | 15        | 0.040     | 6 ±10%             | 0.06 ±20%        | 10-15        | 2.5 ±20% |
| P(PVDF-TrFE)     | 20         | 15        | 0.050     | 6 ±20%             | 0.09 ±20%        | 10-15        | 1 ±20%   |

2.2. Experimental results

Different commercial PVDF and P(VDF+TrFE) samples (summarized in table 1) were measured with the proposed method in 3-1 mode.

To apply deformation samples were glued to a 1 mm thick Plexiglas® substrate and bent with the four-point bending machine. As the curvature radius is constant, the linear deformation $\varepsilon$ of the sample can be calculated as

$$\varepsilon = \frac{h}{2R}$$

where $h$ is the substrate thickness, $R$ is the curvature radius.

Assuming free deformation (stress $T$ is constant) and open electrical circuit (electrical displacement $D$ is constant), the piezoelectric coupling matrix can be written in the following simplified form:

$$S = s^D T + g^D_{ij} D$$

$$E = -g_{ij} T + \beta^T D$$

where $D$ is electric displacement field, $E$ is electric field, $T$ is mechanical stress, $S$ is mechanical strain, $s$ is flexibility, $\beta$ is permeability constant, and $g_{ij}$ is piezoelectric coefficient.

From the second term under our experimental conditions where the switch is kept open during deformation, the electric displacement $D$ is zero, and the voltage can be extracted as:

$$V = -g_{31} \cdot S \cdotYM \cdot t$$

where $t$ is the sample thickness, YM is the Young’s Modulus.
Table 2. Comparison of piezoelectric coefficients from supplier data-sheets and experimentally obtained for different samples.

| Name                          | Data-sheet values | Experimental values |
|-------------------------------|------------------|---------------------|
|                               | $g_{31}$, Vm/N    | $k_{31}$, %         | $g_{31}$, Vm/N    | $k_{31}$, %         |
| LDT1 (28 $\mu$m) MeasSpec     | 0.216            | 12                  | 0.22              | 13                  |
| PVDF (40 $\mu$m) Piezotech    | 0.06 ±20%        | 10-15               | 0.09 (0.16)       | 5.5 (10)            |
| P(PVDF-TrFE) 70-30 (50 $\mu$m) Piezotech | 0.09 ±20%    | 10-15               | 0.4               | 12                  |

The electrical energy produced by the piezoelectric material can be estimated by multiplying the elastic energy by the electromechanical coupling coefficient $k^2$, and is given by equation 3.

$$U_{\text{electrical}} = \frac{1}{2} \cdot Y \cdot M \cdot S^2 \cdot k^2$$  \hspace{1cm} (3)

3. Discussion

Output voltage and the corresponding generated electric energy density as function of applied strain are presented on figures 3 and 4 respectively. The classical linear voltage strain-dependence (as from equation (2)) is confirmed for all samples, but with unusual high voltage values of up to 120V. The slopes of curves reflect at first order the differences in films thickness and also $g_{31}$ coefficients.

Considering the electrical energy density, experimental results also agree with the expected parabolic strain dependence as predicted by equation (3). Consistently with unusual high voltages, one notes remarkable high values of the electrical energy density with about 0.5 to 1 mJ/cm$^3$ for strain of 1%.

Finally, $g_{31}$ voltage coefficient and $k_{31}$ mechanical coupling factor were calculated from results of figures 3 and 4, respectively. The results of calculation are shown in table 2 and compared with those of data sheets.

Figure 3. Voltage output as a function of applied strain in 3-1 mode.

Figure 4. Generated electric energy density as a function of applied strain in 3-1 mode.

The proposed measurement method successfully allows reproducible measurements in quasi-static conditions of the piezoelectric coefficients of the polymer films in real open-circuit conditions. When comparing, one notes $g_{31}$ coefficients being significantly larger than on data...
sheet. It is a clear feature of the P(VDF-TrFE) sample, for example. Considering $k_{31}$ coupling factor, experimental values are in the range of the data sheet, except for the "PVDF (40 µm) Piezotech" sample. The too low value may indicate improper YM value in this case. When using 1.4 GPa instead of 2.5 GPa, $k_{31}$ agrees with expectation (equation (3)). This indicates that $g_{31}$ value is possibly even much larger (shown in brackets in table 2). It is therefore desirable, in order to improve the accuracy of the measurements, to assess with higher precision the YM of the samples prior to piezoelectric measurements. Also, the analytic estimations made for the strain and energy calculation may alter the precision of calculated coefficients. Coupling factors have also been measured by classical frequency-impedance measurements. However, as resonance and anti-resonance with polymers are usually broaden, it does not give adequate precision. Therefore only orders of magnitude can be confirmed.

In terms of measurement accuracy, the main limit of the proposed method is set mostly by the measurement equipment. For instance, in the present work a TREK 370 voltmeter was used which is capable of measuring in 0-3 kV range with 1 V resolution.

4. Conclusion
An improved method for measuring the direct piezoelectric voltage and energy of flexible polymers is reported. Stress is applied with a high precision four-points bending system and voltage is measured with real open-circuit conditions using a mechanical switch. This technic allows exploring direct piezoelectric effect in quasi-static conditions, without use of high-precision equipment nor sophisticated measurement circuits. As a clear feature, we report unusual large strain-induced voltage and electric energy density for PVDF and copolymers. Remarkably high voltage and energy density values of up to 120 V and 1.2 mJ/cm$^3$ were obtained for 40 µm PVDF sample with 0.7 % of strain in 3-1 mode.

Finally, we conclude that the proposed method allows direct piezoelectric coefficients evaluation, which is adequate for generator or harvester considerations. The experimental results of this work suggest that usual voltage coefficient of PVDF and P(VDF-TrFE) copolymers may be underestimated.

References
[1] Guigon R, Chaillout J J, Jager T and Despesse G 2008 Smart Mater. Struct. 17 015039
[2] Vatansever D, Hadimani R L, Shah T and Siores E 2011 Smart Mater. Struct. 20 055019
[3] Canavese G, Stassi S, Cauda V, Verna A, Motto P, Chiodoni A, Marasso S and Demarchi D 2012 Sensors, IEEE pp 1–4
[4] Jiang Y, Shiono S, Hamada H, Fujita T, Higuchi K and Maenaka K 2010 PowerMEMS
[5] Piezo film sensors technical manual URL http://www.meas-spec.com/downloads/Piezo_Technical_Manual.pdf
[6] Piezo sensor - ldt series URL http://www.meas-spec.com/product/t_product.aspx?id=2484
[7] Piezoelectric film technical information URL http://www.piezotech.fr/image/documents/22-31-32-33-piezotech-piezoelectric-films-leaflet.pdf