Experimental Investigation of Electrostrictive Polarization Biased Direct Apparent Piezoelectric Properties in Polyurethane Elastomer Under Quasistatic Conditions

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ABSTRACT: Polyurethane elastomer was recently discovered to demonstrate a very high field induced electrostrictive response. In this work an experimental setup, consisting of an electric circuit and a mechanical system, was designed and constructed for the measurement of the electrostrictive polarization biased apparent piezoelectric response of polyurethane elastomers in a direct piezoelectric effect under quasistatic conditions. The electric circuit design allows the application of a direct current (dc) bias electric field to the sample and the possibility of picking up the generated quasistatic electrical signal separately. The mechanical system provides the function of a vibration source from which the stress and strain of the sample can be measured. Therefore, such effective piezoelectric properties as d_{31} and k_{31} can be measured. The electromechanical coupling coefficient was derived by two different methods. One was from the deduction based on the piezoelectric equations. The other was from the calculation based on the basic definition of the electromechanical coupling coefficient (i.e., through the exact measurement of input mechanical energy and output electric energy). In the latter case, the internal resistance of the sample and the dc bias blocking capacitor were found to be the critical factors for precision determination of the total electrical energy output. The different approaches led to close agreement. The effective d_{31} can be 184 pC/N under a 25 MV/m bias electric field in a 30-μm thick sample, which is much higher than that of typical piezoelectric polymers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2603–2609, 1999

Key words: polyurethane elastomer; piezoelectric polymer; electrostriction polymer; measurement of effective piezoelectric properties

INTRODUCTION

Among the variety of dipolar polymer electrets, poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoroethylene (PVDF–TrFE) exhibited the largest electromechanical coupling effect for a long period. Their ferroelectric natures have already been completely demonstrated. Due to the advantages that these polymers have, such as high mechanical flexibility, low acoustic impedance, low manufacturing cost, and ease of molding into desirable shapes, those polymers and copolymers have found wide application in piezoelectric and pyroelectric devices.[1]

The ferroelectric properties of PVDF mainly result from the polarized crystalline phase, which can be up to a 50% volume fraction dispersed in the amorphous matrix. The higher content of the crystalline phase also makes the elastic compliance much smaller (2 orders) than other polymers

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such as polyurethane elastomer. The introduction of more plasticizer into the PVDF would significantly reduce the piezoelectric response. Only a 20% piezoelectric response remains when the elastic compliance is plasticized to the level of polyurethane elastomer. In such a plasticized state, however, the polymer can sustain an electric field up to 100 MV/m. Consequently, an alternative approach, which is called the field induced electrostrictive effect, to reach high electromechanical response in very soft polymers such as polyurethane elastomer was proposed because in any materials electrostriction strain is proportional to the square of the applied electric field. A strong thickness response coefficient was obtained in polyurethane elastomer under a bias electric field of 25 MV/m, which can be equivalent to the conventional PZT piezoelectric ceramic materials. A large static strain (3%) can also be achieved at the 20 MV/m bias electric field. The data in the above study were derived based on an electrostrictive effect [i.e., applying an electric field to the sample and measuring the displacement (strain)].[2]

The mechanisms of large field induced strain were also studied. The thickness dependence of the strain was investigated. The nonuniform electric field distribution across the sample thickness is considered from the space charge injection.[3] The phase transition influence on the strain and internal activation energy difference between mechanically and nonmechanically related segment motions were investigated.[4,5]

In this study an alternative method was used to evaluate the electrostrictive polarization biased electromechanical response. This method is based on the apparent direct piezoelectric response.[6] The stress was applied to the sample to produce a transverse vibration in a sinusoidal way. The generated electric signal from the sample could be detected from a load resistor. An experimental setup was designed and established, which performed the measurement functions including stress, strain, and electric charge output from which we calculated the parameters of effective piezoelectric response such as the piezoelectric constant and the electromechanical coupling coefficient. Two approaches were used to obtain the electromechanical coupling coefficient. One was from the calculation based on the piezoelectric equation, and the other was calculated from the basic definition of the electromechanical coupling coefficient (i.e., the ratio of the output electric energy to the input mechanical energy).

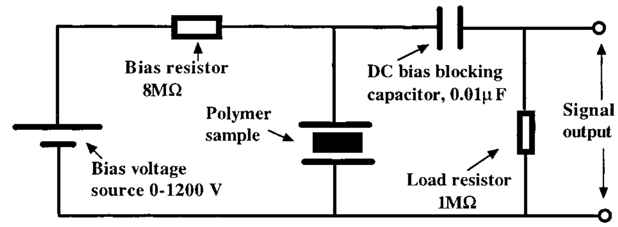

Figure 1 Diagram of the electrical circuit connection.

Both approaches reached results in close agreement. A strong apparent piezoelectric response was observed, which is consistent with the previous studies through the electrostrictive effect.

PRINCIPLE OF MEASUREMENT

Electrical Circuit Connection

The electrical circuit connection is shown in Figure 1. The functions of different parts in the electrical circuit are described in the following. The bias source provides the high direct current (dc) voltage to the sample as the bias electric field. The bias resistor provides the protection to the bias source when the sample is shorted from break down and prohibits the generated signal from the leakage to the bias source. The dc bias blocking capacitor can block the dc bias influence to the load resistor and allow the generated alternating current (ac) signal to flow through to the load resistor, which is read by a lock-in amplifier (SR830DSP, Stanford Research Systems, Inc.).

Mechanical System and Experimental Setup

The mechanical system consisted of the following items: a loudspeaker, a load cell, and a Fotonic sensor. The loudspeaker (6 Ω, Aiwa) produced the vibration force in sinusoidal form, which makes the sample undergo a transverse vibration. The load cell (ELF-TC500, Entran Device, Inc.) measured the force acting on the sample from which we can derive the stress T_1. The Fontonic sensor (MTI 2000, MTI Instruments) measured the transverse displacement of the sample from which we calculate the strain s_1. The schematic view of the experimental setup is shown in Figure 2.

Equations for Piezoelectric Parameters Calculation

The sample is considered equivalent to the vibration mode of transverse extension. Therefore, the

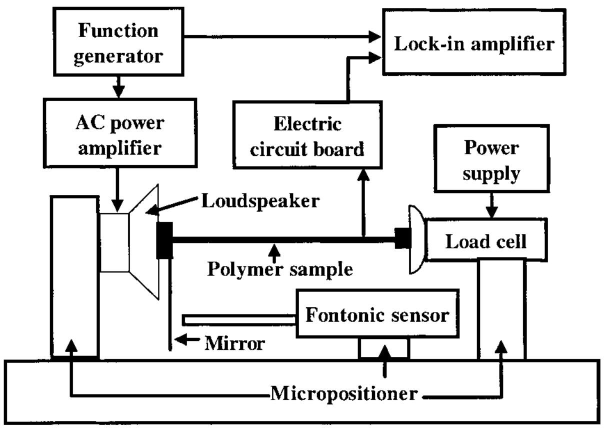

Figure 2 Schematic view of the experimental setup.

parameters can be calculated from the following equations.[7]

The elastic compliance under constant electric field is

$$S_{11}^{E} = \frac{\text{strain}}{\text{stress}} = \frac{S_1}{T_1} \tag{1}$$

and the effective piezoelectric constant is

$$d_{31} = \frac{D_3}{T_1} \tag{2}$$

where the electric displacement D_3 is equal to Q/S, Q is the generated charge, S is the electrode area of the sample, Q is equal to i/ω, i is the current generated in the load resistor, $\omega = 2\pi f$, and f is the vibration frequency.

The effective electromechanical coupling coefficient k_{31} can be expressed by the following piezoelectric equation,

$$k_{31} = \frac{d_{31}}{\sqrt{\varepsilon_{33}^{T} S_{11}^{E}}} \tag{3}$$

where $\epsilon_{33}{}^{T}$ is the dielectric constant under constant stress.

EXPERIMENTAL

The polymer films were prepared by the hot pressing process from pellets provided by Dow Inc. in the 2103-80AE series. Aluminum foils were used as the substrate, frame, and cover layer for pellets during the hot pressing process. After the pressing, the aluminum foils were dissolved by a 5 wt % sodium hydroxide distilled water solution. The aluminum foil free polymer film was cleaned by distilled water and dried naturally. Gold was sputtered on the both surfaces as the electrodes. A super glue was used for fixing the sample to the vibration stage. The thickness of the sample was controlled by the height of the aluminum foil frame. The connection wires were bonded to the sample electrodes by silver epoxy (E solder, conductive adhesives, IMI Insulation Materials Inc.).

RESULTS AND DISCUSSION

Primary Test of Experimental Setup

The experimental setup should have sufficient sensitivity to react to the small variation of the applying force. In order to test this, the electrical output as a function of the strain level at the constant bias field was measured on a thick sample. The results are shown in Figure 3. We can see there is a very good linear relationship between the electrical output signal and the strain even in such a small strain level. This relation also equals the relation between the electric displacement

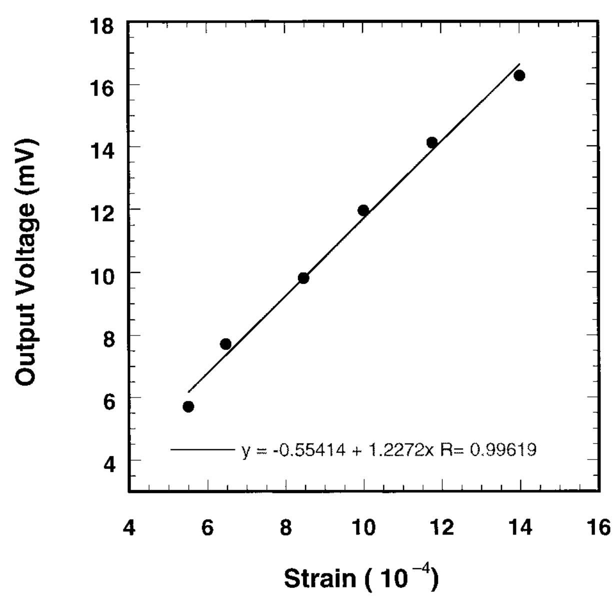

Figure 3 Electric output voltage as a function of strain level. Experimental conditions: sample dimension, 80 × 20 × 0.14 mm; electrode area, 70 × 12 mm; bias electric field, 3 MV/m; bias resistor, 8 MΩ; load resistor, 1 MΩ; vibration frequency, 5 Hz; dc bias blocking capacitor, 0.01 μF.

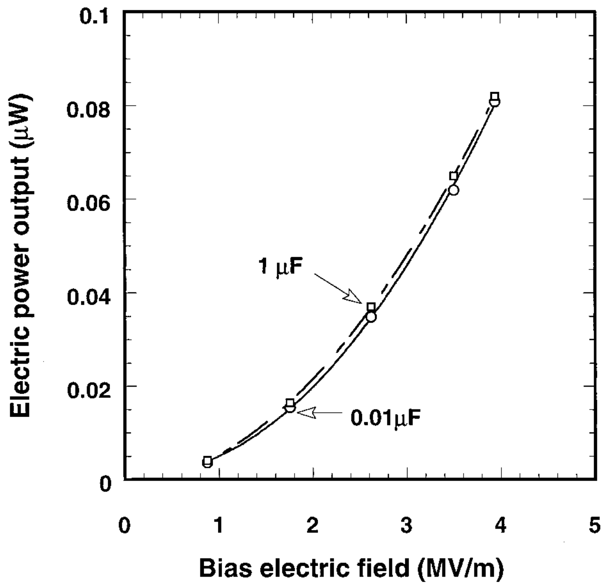

Figure 4 Comparison of electric power output of different dc bias blocking capacitors. Experimental conditions: sample dimension, 60 × 30 × 0.08 mm; electrode area, 20 × 35 mm; vibration frequency, 10 Hz; vibration displacement, 0.93 mm; vibration force, 0.76 N; dc bias blocking capacitor, 0.01 and 1 μF; bias resistor, 8 MΩ.

and external stress. The linear relationship means the electromechanical response is the typical feature of the piezoelectric response.

There will be always some leakage of generated charge to the bias resistor. If the dc bias blocking capacitor is too small, the impedance to the ac current would be very large. If the dc bias blocking capacitor is too large, the time constant in the load circuit would be high. It is necessary to choose the appropriate capacitors for the comparison. In the acceptable range, we chose 0.01 and 1 μF as the dc bias blocking capacitor from which we can see how much the dc bias blocking capacitor will influence the charge output signal. Figure 4 gives the comparison of the generated energy output on the load resistor as a function of the bias electric field with different dc bias blocking capacitors and the related experimental parameters. Although there is some deviation of the power output curves, the error is so small that we can ignore the difference in a big range of capacitor values (the difference of impedance is 100 times in the above comparison). That also means the leakage of charge is only in a very small portion so we could ignore it in the calculation. The square nature of the power output as a function of the applied bias field is obviously seen from the curve.

Effective Piezoelectric Parameters Measured on 30-μm Thick Sample

A 30-μm thick sample was used for comprehensive measurement of its effective piezoelectric properties because the thinner sample can be put into more uniform distribution vibration and a higher bias electric field can be applied easily. Under a constant strain level (i.e., constant stress) the dependence of the effective piezoelectric constant d_{31} as a function of the bias electric field was measured. Figure 5 shows the results and corresponding experimental conditions.

At the maximum bias electric field (25.26 MV/m) of this investigation, the effective d_{31} can be 184 pC/N. The corresponding effective electromechanical coupling coefficient k_{31} can be calculated from eq. (3), which is equal to 7.67% (where $s_{11}{}^E$ is 9.3 × 10^{-8} m^2/N and $\epsilon_{33}{}^T$ is 7 × 8.85 × 10^{-12} F/m).

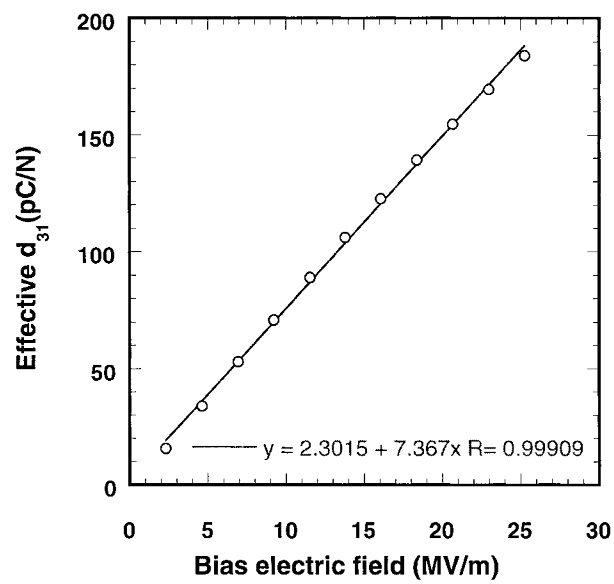

Figure 5 Effective piezoelectric constant d_{31} of 30-μm thick sample as a function of bias electric field. Experimental conditions: sample dimension, 42 × 20 × 0.03 mm; electrode area, 40 × 12 mm; external force, 0.053 N; stress, 8.8 × 10^4 N/m^2; transverse displacement, 0.343 mm; strain, 0.82%; elastic compliance, $s_{11}{}^E = s/T_1 = 9.3 \times 10^{-8}$ m^2/N; mechanical energy input, $W_M = 2 \times 3.14 \times 10 \times 0.343 \times 10^{-3} \times 0.053 = 1.141 \times 10^{-3}$ W.

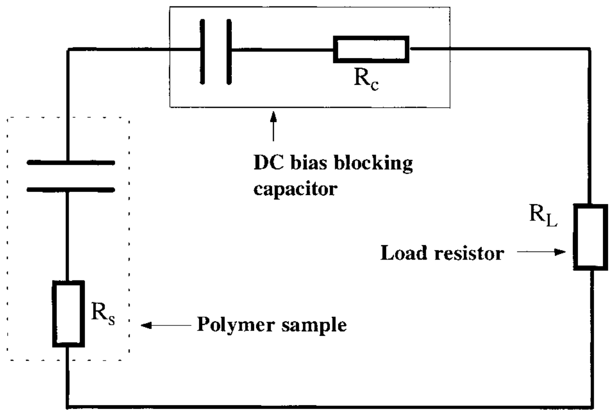

Figure 6 Equivalent circuit for electric energy consumption.

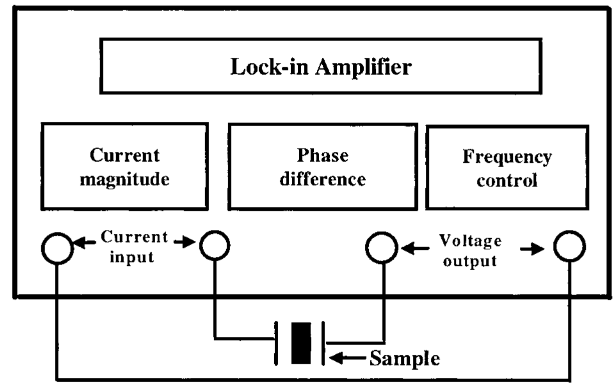

Figure 7 Schematic diagram of the electronic connection for the internal resistance measurement.

Alternative Way to Acquire Electromechanical Coupling Coefficient

The current i in the load resistor is the critical data for the calculation of the effective d_{31} by the piezoelectric equation. In this case, we do not need to consider the internal resistance of the polymer and the dc bias blocking capacitor.

We can also directly calculate the electromechanical coupling coefficient k from its basic definition because this measurement system can acquire the data needed for the calculation

$$k^2 = W_E/W_M = \text{electric energy output/mechanical energy input} \quad (4)$$

from eq. (4).

The mechanical energy W_M input can be calculated from the product of the velocity and the applied force in a final unit of watts. The W_M is equal to 1.141×10^{-3} W for the 30-μm thick sample.

In order to get the electric power consumed in the loop, we need to know the internal power consuming resistance of the sample and the dc bias blocking capacitor. The right loop of Figure 1 can be redrawn to an equivalent circuit shown in Figure 6.

The operation frequency of the sample is 10 Hz. The dielectric loss is very difficult to determine by the conventional LCR meter at such low frequency. In this experiment, a method was designed to determine the internal resistance of the sample and the dc bias blocking capacitor by using a lock-in amplifier. The internal signal source of the lock-in amplifier can be applied to the sample. The current and the phase can be measured. Figure 7 shows the schematic diagram of the electronic connection for the internal resistance measurement.

The electrical impedance of the dielectric component can be expressed in the following equation[8]:

$$Z = V/I = Z_m(\cos\theta + i\sin\theta) = Z_m\cos\theta + iZ_m\sin\theta \quad (5)$$

where V is the applied voltage, I is the current, and θ is the phase difference between the voltage and the current. The resistance part $Z_m \cos\theta$ is the internal resistance that consumes the energy.

The measurements were carried out on the 30-μm thick sample and 0.01 μF dc bias blocking capacitor. The results are shown in Table I.

The electric energy output is composed of several parts: electrical energy consumed in the load resistor, electrical energy consumed in the internal resistance of the polymer, and electrical en-

Table I Internal Resistance of 30-μm Thick Polymer Sample and 0.01-μF dc Bias Blocking Capacitor

	30-μm Thick Sample	dc Bias Blocking Capacitor
Applied voltage (V)	0.2	0.2
Frequency of voltage (Hz)	10	10
Current (nA)	0.9	0.858
Phase θ (°)	−94.43	89.52
Internal resistance (MΩ)	17	1.95

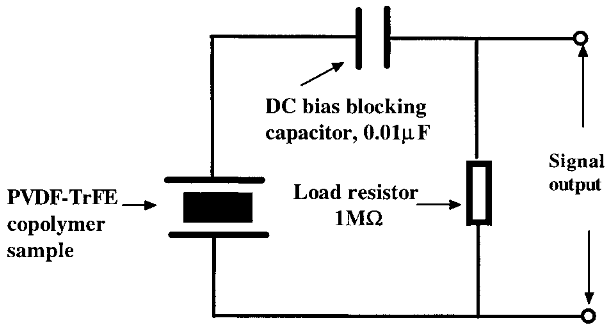

Figure 8 Electrical circuit connection for PVDF–TrFE copolymer measurement.

ergy consumed in the internal resistance of the dc bias blocking capacitor.

The total electrical energy consumed can be calculated by the equation

$$W_E = i^2(R_s + R_c + R_L) \tag{6}$$

where i = output voltage of the load resistor (V)/resistance of load resistor (Ω).

In this experiment, at the 25.26 MV/m bias electric field the total electrical energy output is

$$W_E = (0.488/10^6)^2(17 \times 10^6 + 1.95 \times 10^6 + 1 \times 10^6) = 4.75 \times 10^{-6} W$$

so

$$k^2 = W_E/W_M = 4.75 \times 10^{-6}/1.141 \times 10^{-3} = 4.16 \times 10^{-3}$$

$$k = 0.064 = 6.4\%$$

This value is very close to the result (k_{31} = 7.67%) calculated from the piezoelectric equation, eq. (3).

Comparison Measurement Performed on PVDF–TrFE Copolymer

In order to confirm the measurement system, a polymer with well-known piezoelectric properties was used for the test. In this experiment, 50/50 PVDF–TrFE copolymer was used. PVDF–TrFE 50/50 film was prepared by hot pressing. The poling conditions were a 60 MV/m electric field at 70°C in silicon oil for 20 min and cooling the sample with the voltage on. The sample was 50 × 10 × 0.053 mm and had an electrode area of 40 × 6 mm. The electrical circuit connection for the measurement is shown in Figure 8.

Actually, we did not need to keep the dc block capacitor. Keeping it in the circuit was just to keep the environment the same as in the previous experiment.

Three different magnitude stresses were used for the measurement. The measured results are listed in Table II.

The reported d_{31} value for PVDF–TrFE copolymer is about 15–30 pC/N because the properties of the polymer are highly dependent on the processing conditions.[9] Our result was in this range. We might have gotten a higher value for PVDF–TrFE if we had used a higher power loudspeaker because the much higher stiffness of the PVDF–TrFE copolymer makes it very difficult to uniformly stretch the sample.

CONCLUSIONS

The measurement performed from a response in a direct apparent piezoelectric effect also provides the evidence for a strong electrostrictive polarization biased electromechanical response in polyurethane elastomer. The effective d_{31} value can be 184 pC/N under 25 MV/m bias electric field, which is comparable to the commercial PZT ceramics. The introduced experimental setup can offer the following advantages:

1. the system is a simple configuration and consists of conventional laboratory equipment,
2. the data derived by this system are of macroscale magnitude so that the accuracy of the measurement can be very high, and
3. the electromechanical coupling coefficient can be confirmed by a different approach from which we can recheck the electrical and mechanical parameters. Those advantages make this system an efficient way to

Table II Piezoelectric Constant of 50/50 PVDF–TrFE Copolymer under Different Stress Levels

Stress × 10^6 (N/m^2)	Output Voltage (mV)	d_{31} (pC/N)
1.23	342	18.44
2.02	502	16.4
2.64	650	16.32

characterize the piezoelectric properties of soft polymer in a quick and accurate way.

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