JOURNAL OF Applied Polymer SCIENCE

# PVDF piezoelectric voltage coefficient *in situ* measurements as a function of applied stress

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**ABSTRACT:** Direct piezoelectric $g_{31}$ voltage coefficient was measured *in situ* as a function of applied tensile stress for films of polyvinylidene fluoride (PVDF). Measurements were performed under quasi-static conditions with applied strain rates of 0.5–1.5 mm/min for strains up to 12%. Open-circuit voltage was measured with a contact-less electrostatic voltmeter. Obtained results show a strong dependence of the $g_{31}$ coefficient of mono-oriented PVDF films on the applied stress, with a maximum value of the coefficient in the transition region between elastic and plastic deformation zones. The effect of sample geometry on the apparent $g_{31}$ coefficient is shown and discussed. The anisotropy of the piezoelectric effect is studied by means of $g_{31}$ and $g_{32}$ measurements. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43248.

**KEYWORDS:** dielectric properties; mechanical properties; properties and characterization

Received 7 August 2015; accepted 23 November 2015
**DOI: 10.1002/app.43248**

## INTRODUCTION

Polyvinylidene fluoride (PVDF), or simply PVDF, is a chemically stable thermoplastic fluoropolymer synthesized by the polymerization of vinylidene difluoride. The semi-crystalline piezoelectric PVDF polymer shows a complex structure and can present five distinct crystalline phases: $\alpha$, $\beta$, $\gamma$, $\sigma$, and $\varepsilon$. Different phases are related to different chain conformations: TTT (all trans) planar zigzag for the $\beta$-phase, TGTG′ (trans-gauche-trans-gauche) for the $\alpha$ and $\sigma$ phases and $T_3GT_3G'$ for $\gamma$ and $\varepsilon$ phases.[1] The $\beta$-phase is the one with the highest dipolar moment per unit cell, when compared to the other phases,[2] and it is the one that gives the PVDF its piezoelectric properties.

Different strategies have been developed to obtain the piezoelectric phase of PVDF, mainly focusing on the development of specific processing procedures (mechanical stretching, high pressure, external electric field, ultra-fast cooling) and the inclusion of specific fillers ($BaTiO_3$, clay, ferrite nanoparticles etc.).[1] In particularly, it has been shown that the content of piezoelectric $\beta$-phase in PVDF increases with elongation and heating.[3–6] It was shown to be particularly sensitive for the tensile strain rate.[4,5] However, the pronounced effects were only shown at high strain ranges (100–600%) and temperatures around 80°C. Little discussion was given to effects at smaller strains, and no direct effect of strain on the piezoelectric voltage coefficient $g_{31}$ was measured.

Usually, piezoelectric coefficients of ceramic thin films are measured with well-established methods, such as optical interferometry analysis of the reverse piezoelectric effect[7–10] or by frequency measurement methods.[7,11] Consequently, $d_{33}$ or $d_{31}$ piezoelectric charge coefficients are usually extracted from the measurement, from which $g_{33}$ or $g_{31}$ voltage coefficients can be further recalculated.

Piezoelectric measurements of PVDF films are less established. Similar techniques have been reported, including laser interferometry,[12] low-frequency surface acoustic waves,[13] bimorph bending,[14] and piezoresponse force microscopy.[15] All these methods measure directly only the charge coefficients $d_{ij}$, and often require expensive and complex measurement equipment. However, the $g_{ij}$ voltage coefficient is representative for booming applications such as sensors and energy harvesting. It is measured in Vm/N and it shows directly what voltage is generated by a piezoelectric under applied force.

PVDF manufacturers usually provide the $g_{31}$ and $g_{33}$ values, but never give details on how these values are measured. Our group has previously reported a method of measuring directly piezoelectric voltage coefficients of flexible polymers using four-point bending system.[16] It allows direct measurement of PVDF $g_{31}$ coefficient under open-circuit conditions, but relies on the supplier's datasheet values of Young's modulus, which are often given with low precision (i.e., ±30% confidence interval[17,18]).

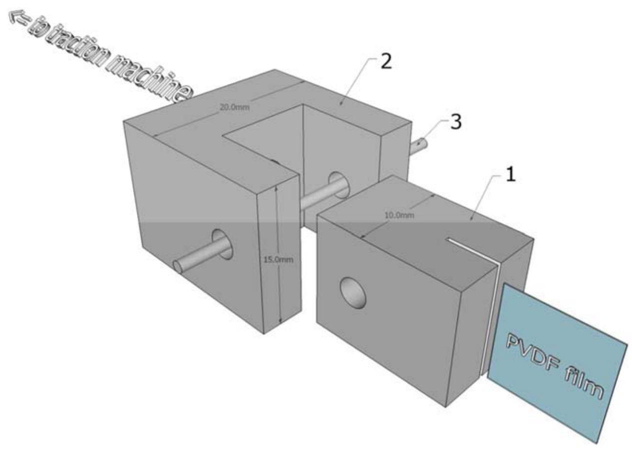


**Figure 1.** Schematic drawing of the clamps used for PVDF thin films traction tests. The PVDF film is glued inside part 1, which is then fixed inside part 2 with a cylindrical rod 3. Part 2 is screwed to a traction machine. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In addition, the strain developed by the bending method was insufficient to observe any effects on the piezoelectric coefficient. In this work, we introduce a method for *in situ* measurement of PVDF $g_{31}$ piezoelectric voltage coefficient as a function of tensile stress, performed under quasi-static and open-circuit conditions, independently from the datasheet parameters.

## EXPERIMENTAL

### Sample Preparation

The PVDF film samples for tensile experiments were prepared in accordance with the ISO 527-3:1995 standard[19], which indicates sample geometry and testing conditions.

To hold the samples firmly in place during measurements, special clamps adapted for thin films, shown in Figure 1, were fabricated in a 3D printer from ABS plastic. The PVDF film is glued with cyanoacrylate glue inside an opening in part 1. Parts 1 and 2 are assembled by means of a pin (part 3), which allows part 1 to freely rotate inside part 2. Part 2 is connected directly to the tensile machine by means of a screw. The design of the clamps allows firm fixation of thin PVDF samples with no slipping during stretching, while the tensile strength is applied homogeneously along the film cross-section and no shear forces appear.

PVDF films from two suppliers were used: uniaxially oriented 110 µm thick films from Measurement Specialties, having silver ink metallization, and biaxially oriented 40 µm thick films from Piezotech with no metallization. Samples of rectangular shape with lengths from 20 to 30 mm and widths varying from 5 to 15 mm were cut manually from a large sheet of material using a cutter knife. Sample geometries are synthesized in Table I. Next, samples were glued into the clamps and left to dry for at least 12 h. To measure the generated voltage, a thin metal wire was glued with conductive epoxy (CircuitWorks CW2400, $P < 0.001$ Ω cm) to each surface of the sample, whether metallized or not. When the surface is not metallized, a thin layer of conductive silver grease (CircuitWorks CW7100, $P < 0.01$ Ω cm) was applied. The use of conductive grease allowed to perform measurements up to 10% of strain without any degradation of the electrodes. Use of tried and trusted low resistivity, silver charged conductive epoxy and grease ensured Ohmic contact at the interfacial regions.

**Table I.** Synthesis of Sample Geometries with Experimentally Measured $g_{31}$ Piezoelectric Coefficients and Young's Moduli for Samples with Different $L$:$W$ Ratios

| LxW (mm) | Ratio $L$:$W$ | Max $g_{31}$ (Vm/N) | YM (MPa) |
|---|---|---|---|
| PVDF MeasSpec 110 µm | | | |
| 20 × 15 | 1.3 | 0.28 | 1300 |
| 20 × 5 | 4 | 0.24 | 1900 |
| 30 × 5 | 6 | 0.24 | 1900 |
| 40 × 5 | 8 | 0.23 | 2100 |
| Datasheet[18] | | 0.216 | 3000 ± 30% |
| PVDF Piezotech 40 µm | | | |
| 20 × 15 | 1.3 | 0.12 | 1800 |
| 30 × 10 | 3 | 0.09 | 2200 |
| 20 × 5 | 4 | 0.067 | 2300 |
| 30 × 5 | 6 | 0.065 | 2150 |
| 40 × 5 | 8 | 0.07 | 2400 |
| Datasheet[17] | | 0.056 ± 20% | 2500 ± 20% |

Supplier datasheet values are shown for reference.

A ready-to-measure sample in clamps with attached electrodes is shown in Figure 2.

### Experimental Procedure

A tensile machine from MTS was used to strain the films. An integrated force sensor allowed for the direct stress calculation in the film. For a uniform force/stress distribution, the stress is given by the following equation:

$$\sigma = \frac{F}{w \cdot h} \tag{1}$$

where $\sigma$ is the stress (Pa), $F$ is the force (N), $w$ is the width (m), and $h$ is the thickness of the film (m).

NB:this formula is only valid for high form factor samples (length:width > 4), where the uniform stress hypothesis is respected.


**Figure 2.** Sample mounted in clamps with attached electrodes for piezoelectric strain measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

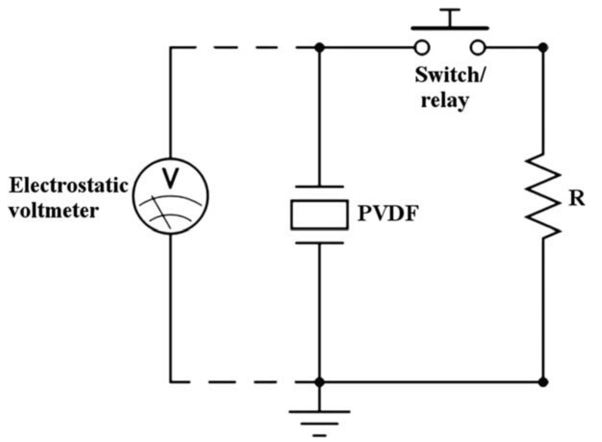


**Figure 3.** Simplified measurement circuit of the piezoelectric voltage.

Film strain was calculated from the linear displacement sensor of the machine by:

$$\varepsilon=\frac{\Delta l}{l} \tag{2}$$

where $\Delta l$ is the linear displacement (m) and $l$ is the length of the film (m).

A simplified measurement circuit is shown in Figure 3. The voltage output was measured by a contact-less electrostatic voltmeter (Trek 370), connected directly to the sample. As was previously shown,[14] the use of such a voltmeter enables precise measurement of the piezoelectric voltage without parasitic leakage or loss into the measurement circuit. A mercury relay was used to switch on the circuit to discharge the PVDF samples when necessary.

The measurement procedure was automatized by a LabView script, which synchronized mechanical force and strain measurements of the tensile machine with voltage measurements. It also controlled the relay open/closed states.

During the measurement, the samples were strained with a constant loading speed and their open-circuit voltage output was registered as a function of stress. For such experimental conditions, the piezoelectric matrix can be written in terms of constant electric displacement $D$ and stress $T$, as expressed on eq. (3). Under open-circuit conditions, where $D$ is zero, the $g_{31}$ coefficient was calculated [using eq. (4)] from the slope of stress-voltage dependence with known film thickness. The thickness was measured prior to voltage measurements and was assumed constant during stretching, as its variations due to Poisson ratio would be <2% in the measurement range.

$$\begin{cases} S=s^D T+g_{31}^t D \\ E=-g_{31} T+\beta^T D \end{cases} \tag{3}$$

where $S$ = strain, $T$ = stress, $D$ = electric displacement, $E$ = electric field, $\beta^{\mathrm{T}}$ = permeability at constant stress, and $s^{\mathrm{D}}$ = flexibility at constant electric displacement.

$$|g_{31}|=\frac{E}{T}=\frac{V}{t\cdot T} \tag{4}$$

where $V$ = voltage and $t$ = sample thickness.

The $g_{31}$ coefficient describes the change in electric field when stress is changed. It is measured by applying a known stress and measuring the changes in open-circuit electric field. Strictly speaking, to compare with literature values, the g coefficient should only be calculated in the linear elastic region of the stress-strain curve. However, since PVDF is of interest in flexible applications, where it is possible to stay out of the linear elastic region, we have explored values of strain, which go beyond this linear elastic region. We will nonetheless still refer to the "*g* coefficient" as a coefficient or proportionality between the applied stress and the induced electric field, even beyond the elastic limit of the material.

The relay was closed and opened periodically, meaning that the observed voltage would repeatedly rise to a certain value and then drop to zero. For most of the samples, the switching period was set to 2 s, which was a compromise between piezoelectric voltage generation and voltage decay due to self-discharge.

The straining speed was kept constant during the measurement, and, depending on the sample length, was set between 0.5 and 1.5 mm/min. The measurements were performed at room temperature of 23°C and relative humidity of ~46%.

## RESULTS AND DISCUSSION

Typical measured voltage as a function of stress is shown on Figure 4. The blue periods correspond to the open relay state and the red one to the closed state. Voltage peaks are reached just before the relay state changes from open to closed, followed by a subsequent voltage drop.

The calculated $g_{31}$ coefficient as a function of applied stress for a Piezotech sample with Length:Width ($L$:$W$) ratio of 4 is shown on Figure 5. The stress-strain curve is shown superimposed. The value given by the supplier is $g_{31}$ = 0.056 Vm/N. As can be seen from the graph, the calculated $g_{31}$ values at low stress and strain are about 0.04 Vm/N which is below the datasheet value and out of the indicated confidence interval (±20%). With increasing stress, $g_{31}$

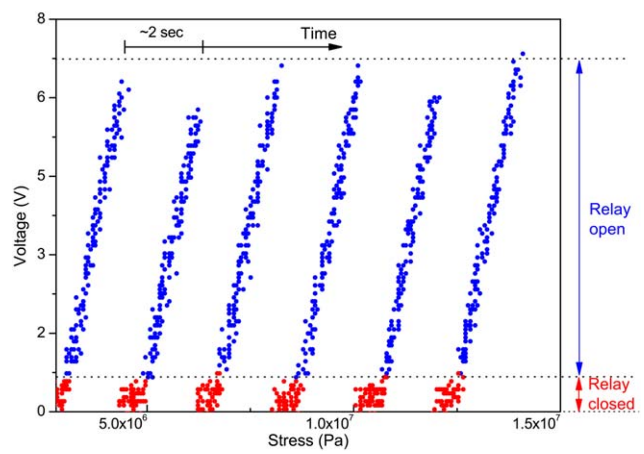


**Figure 4.** Typical piezoelectric voltage measurement as a function of applied stress. The voltage drops to zero every time the relay closes, and stays zero until the relay is opened. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

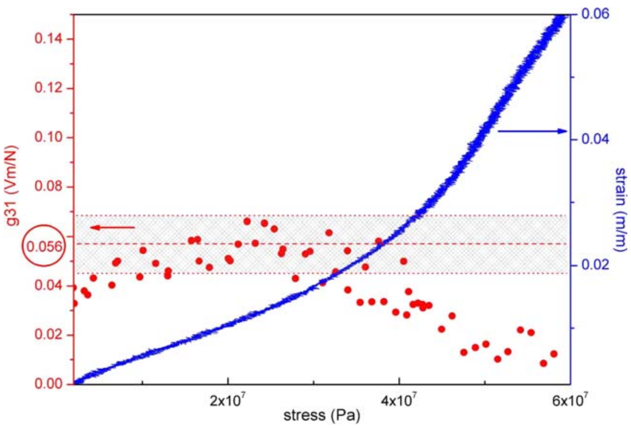


**Figure 5.** Piezoelectric $g_{31}$ voltage coefficient (symbols) and strain (lines) as a function of applied stress for the Piezotech sample with $L : W$ ratio of 4. The supplier datasheet value for $g_{31}$ is 0.056 ± 20% Vm/N. The confidence interval is shown by dotted lines. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

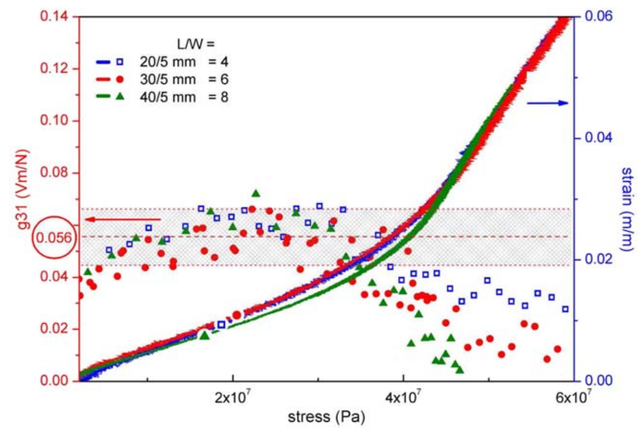


**Figure 6.** Piezoelectric $g_{31}$ coefficient (symbols) and strain (lines) as a function of applied stress for Piezotech samples with $L : W$ ratios of 4, 6, and 8, respectively. Datasheet value of $g_{31}$ is 0.056 ± 20% Vm/N. The confidence interval is shown by dotted lines. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increases until it reaches a maximum of 0.065 Vm/N and then gradually decreases to zero. Remarkably, the maximum value of $g_{31}$ is situated in the middle of the elastic region, and the decrease corresponds to the change in the stress-strain slope, representing the beginning of the transition between elastic and plastic regions, in this case, at 25–30 MPa and 1–1.5% strain. Within the strain interval between 0.5 and 2% strain, the $g_{31}$ values stay inside the datasheet confidence interval of 0.056 Vm/N ± 20%.

Figure 6 shows the $g_{31}$ coefficient versus stress dependence for three Piezotech samples having different $L$:$W$ ratios of 4, 6, and 8. Independently of the geometrical parameters, the main trend is visible for all the samples: at low stress and strain $g_{31}$ is somewhat lower than the datasheet value, it then increases with stress until its maximum value of around 0.065 Vm/N, and then gradually decreases. All three samples reach their maximum $g_{31}$ value at around 25 MPa and 1.5% strain, which correspond to the middle of the elastic deformation zone. The maximum is followed by a short plateau where the $g_{31}$ value stays constant. The length of the plateau is visually independent on the sample $L$:$W$ ratio. Once in the plastic region, the behavior of $g_{31}$ coefficient is clearly impacted by the sample's geometrical parameters: the lower the $L$:$W$ ratio, the slower the $g_{31}$ coefficient decreases with stress. The stress-strain curves are also slightly different according to the samples, however with no significant change in the Young's modulus value and the elastic limit.

The measured coefficient values are situated inside the confidence interval of the datasheet value from strains of 0.5% to around 2.5%. At lower strains however, once more the measured values are lower than expected, which indicates that for practical applications it would be advisable to prestrain the PVDF material to effectively exhibit its expected piezoelectric performance.

If we now compare the Piezotech samples with much lower $L$:$W$ ratios, down to 1.3 (shown on Figure 7) we can distinctly see the influence of the sample geometry on the $g_{31}$ coefficient apparent values and behavior. Wider samples with low $L$:$W$ ratios (thus closer to a square than to a rectangle) show $g_{31}$ values starting from 0.06 Vm/N and going up to 0.14 Vm/N. Their stress-strain curves are significantly higher, meaning that for the same applied strain they undergo much lower stress than previous samples. At low $L$:$W$ ratios, the apparent Young's modulus decreases, and the transition between the elastic and plastic zones is much less noticeable. This apparent decrease happens because wider samples with low $L$:$W$ do not respect the geometry requirements in tensile experiments for homogeneous stress distribution; some parts of the strained sample may experience higher stress than others, and eq. (4) will lead to false and overestimated $g_{31}$ values. It is therefore not the material parameters themselves that change with sample size, but only the apparent measured values, which are impacted by nonhomogeneous stress distribution in such samples.

The 110 μm MeasSpec PVDF has an altogether different behavior (Figure 8) with a more pronounced increase of the $g_{31}$ value

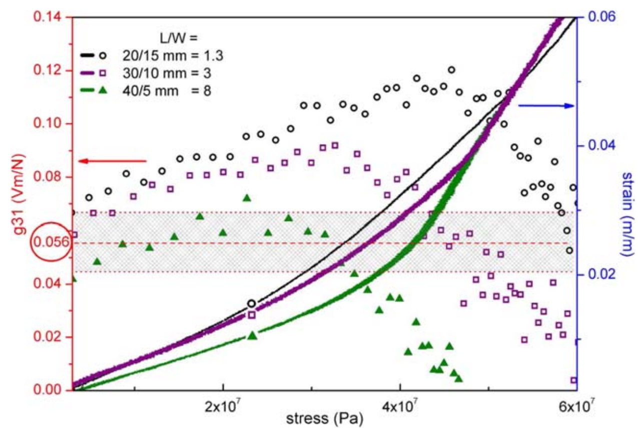


**Figure 7.** Piezoelectric $g_{31}$ coefficient (symbols) and strain (lines) as a function of applied stress for Piezotech samples with various $L$:$W$ ratios from 1.3 to 8. Datasheet value of $g_{31}$ is 0.056 ±20% Vm/N. The confidence interval is shown by dotted lines. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

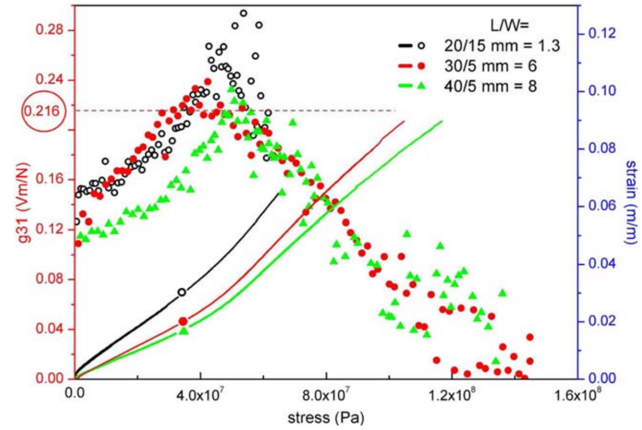


**Figure 8.** Piezoelectric $g_{31}$ coefficient (symbols) and strain (lines) as a function of applied stress for MeasSpec samples with $L$:$W$ of 1.3, 6, and 8. Datasheet value of $g_{31}$ is 0.216 Vm/N. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

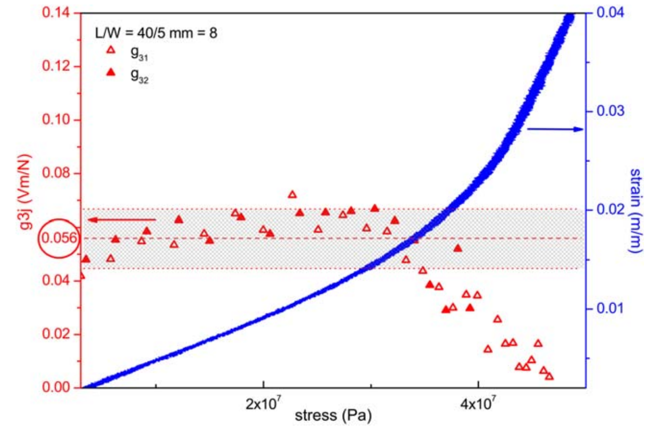


**Figure 9.** Anisotropy study of Piezotech samples. Comparison of $g_{31}$ and $g_{32}$ versus applied stress. Datasheet value of $g_{31}$ is 0.056 Vm/N. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with stress. $g_{31}$ increases with increasing stress and reaches its maximum around the beginning of transition between elastic and plastic regions at 60 MPa and 3% strain. The influence of the sample geometry is less clear than on the Piezotech samples: wide and narrow samples have similar $g_{31}$ values and similar stress dependence. The maximum $g_{31}$ values of the $L$:$W = 8$ and $L$:$W = 6$ samples are near the datasheet value. The wide sample with $L$:$W = 1.3$ has higher $g_{31}$ values for the same reasons as proposed before, namely for nonhomogeneous stress distribution. Since the confidence interval for $g_{31}$ is not provided by the supplier, we cannot affirm until what stress the measured values are reasonable.

In contrast with the Piezotech samples, the $g_{31}$ values at low stress for the MeasSpec samples are significantly lower than the datasheet value and they stay low until a relatively high strain is applied. In other words, to reach the announced datasheet value of the piezoelectric coefficient, the sample has to be pre-strained to about 3%, which is the limit of the linear elastic region.

Table I summarizes the measured $g_{31}$ coefficients and Young's moduli for different samples. As a general trend, long and narrow samples with higher $L$:$W$ ratios are closer to the datasheet values than the shorter and wider samples. All samples with $L$:$W$ ratio $< 4$ (Piezotech or MeasSpec) fell outside the datasheet confidence intervals for Young's modulus and $g_{31}$ coefficient, because of the invalid stress homogeneity hypothesis. This shows the importance of an appropriate choice of material geometry for the testing procedures as well as for the applications in energy harvesters, sensors, or actuators, to ensure that the working hypothesis, in this case homogeneous stress distribution in the sample, is valid.

Without additional micro-structural studies, it is difficult to argue on the origins of the observed phenomena of the increase of $g_{31}$ in the elastic region and its decrease in the plastic region. Reorientation of the $\beta$-phase chains from perpendicular to parallel to the stress orientation within the plastic region and a decrease in the degree of crystallinity[20,21] may contribute to the overall decrease of the piezoelectric properties. In addition, nonlinearity of the elastic modulus during stretching may lead to nonlinearity of the piezoelectric coefficients.[22] This is nonetheless an important experimental result, since it highlights the benefits of prestraining the PVDF to obtain higher voltage output.

It is important to note that repeatability of the measurements on one sample was only obtained if the sample was deformed within the elastic region. Once the plastic deformation has been reached, the sample suppress microstructure is irreversibly changed; if the measurement cycle is then repeated, the $g_{31}$ will differ from its initial values.

### Anisotropy Study

The PVDF material is known for its anisotropic properties of the piezoelectric effect.[13,23–25] The piezoelectric performance along direction 2 of uniaxially oriented films is lower than along direction 1, which comes from the anisotropic semicrystalline structure of PVDF. This is attributed to processes occurring in the crystalline regions and in their interfaces with the amorphous surrounding.[23] In biaxially oriented films the anisotropic effects are eliminated.[17,24]

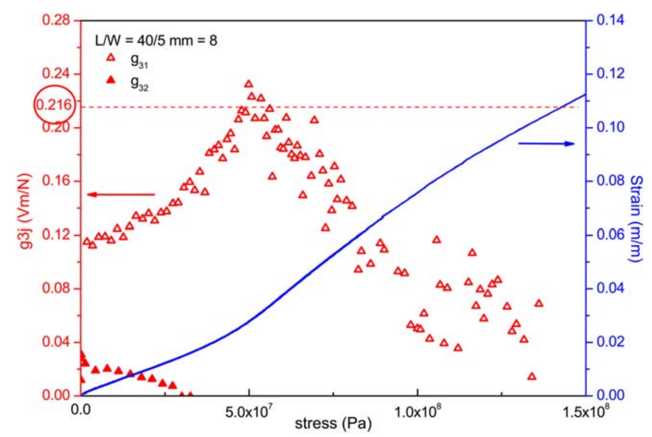


**Figure 10.** Anisotropy study of MeasSpec samples. Comparison $g_{31}$ and $g_{32}$ vs. applied stress. Datasheet value of $g_{31}$ is 0.216 Vm/N. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To study the directional anisotropy of the piezoelectric effect, additional samples with $L$:$W$ ratio of 8 were cut from PVDF sheets in a perpendicular direction compared with the previous samples. This allows extracting the $g_{32}$ coefficient in addition to previously measured $g_{31}$.

Figures 9 and 10 show $g_{31}$ and $g_{32}$ coefficients as a function of stress for Piezotech and MeasSpec samples, respectively. Biaxially stretched Piezotech samples present no anisotropy, with the $g_{3j}$ coefficient being practically independent of the direction of applied stress. On the contrary, the uni-axially stretched MeasSpec samples present a high level of anisotropy, with $g_{32}$ being 10 times lower than $g_{31}$.

The anisotropy characteristic of the material is closely connected with its $g_{3j}$ geometry sensitivity. When stretched in one direction, the material is compressed in perpendicular directions due to Poisson effect. For a piezoelectric material, this means that the observed $g_{31}$ coefficient is always a sum of $g_{31}$, $g_{32}$, and $g_{33}$ coefficients. The MeasSpec PVDF has much lower $g_{32}$, which makes it less sensitive to geometry form-factor of samples. The Piezotech PVDF has equivalent values of $g_{31}$ and $g_{32}$, which makes it highly sensitive to sample geometry.

## CONCLUSIONS

We have presented experimental results of *in situ* direct measurements of the piezoelectric $g_{31}$ voltage coefficient of PVDF commercial films. A strong dependence of the $g_{31}$ coefficient on the applied strain is reported. Uniaxially oriented PVDF showed a maximum value of $g_{31}$ coefficient in the middle of elastic region of the material. Biaxially oriented PVDF showed a maximum $g_{31}$ value near the transition from elastic to plastic deformation regions.

The $L$:$W$ ratio of the rectangular samples significantly influenced the measured apparent $g_{31}$ coefficient, which was apparently higher for the wider and shorter samples (smaller $L$:$W$ ratio). Since material parameters should not depend on external dimensions, this geometry impact leads to a measurement artifact, coming from underestimated stress (nonuniform stress distribution), which leads to overestimated $g_{31}$ values. This highlights the importance of an appropriate choice of material geometry for direct piezoelectric measurements and further applications.

The uniaxially oriented PVDF has shown strong piezoelectric anisotropy, with $g_{32}$ at low strain being 5 times lower than the measured $g_{31}$, and 10 times lower than the data-sheet $g_{31}$ value. The biaxially oriented PVDF has shown isotropic behavior, with $g_{31}$ and $g_{32}$ being identical in the measurement range of 0–2.5% strain.

Finally, the obtained results suggest that the datasheet values of the piezoelectric voltage coefficients, provided by the material manufacturers, might be overestimated at low stress. When strained, $g_{31}$ is increased, suggesting that pre-strain becomes an important parameter for applications. Both commercial grades of PVDF from Piezotech and MeasSpec had to be strained from 0.5 to 3% to observe the announced data-sheet values.

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