Ferroelectric Polymers for High Pressure and Shock Compression Sensors

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ABSTRACT

Ferroelectric polymers (PVDF) with well-defined and precisely known electrical properties are now routinely available from commercial sources. Electrical processing with the Bauer cyclic poling method can produce individual films with a well-defined remanent polarization up to 9 \( \mu \text{C/cm}^2 \). These polymers provide an unusual opportunity to study the structure and physical properties of materials subjected to shock loading. The behavior of PVDF has been studied over a wide range of pressures using high-pressure shock loading and has yielded well-behaved reproducible data up to 25 GPa in inert materials. In these impact experiments between 0 and 12 GPa, identical impactor and sample materials (sapphire, quartz, Kel-F and Cu) were used to determine the PVDF piezoelectric response. The use of different materials has allowed us to vary the loading path. But over 12 GPa, only Cu impactor and sample materials were used. These observations raise naturally the question of the loading path dependence of the piezoelectric response of PVDF at higher shock pressure levels. Consequently, studies of the piezoelectric behavior of PVDF gauges under impact loading using a two-stage light gas gun have been conducted recently. At high pressure, shock-induced polarization or electrical charge can be released inside the shock-compressed materials (i.e., polymers, crystals…). A solution using an appropriate electrical shielding has been identified and applied to PVDF for these studies. Results show that the PVDF response appears independent of the loading path up to 30 GPa.

An application of PVDF for Hugoniot measurements of High Explosives (H.E.) is described. Furthermore, shock pressure profiles obtained with in situ PVDF gauges in porous H.E. (Formex) in a detonation regime have been achieved.

\( \text{P(VDF-TrFE)} \) copolymers exhibit unique piezoelectric properties over a wide range of temperature depending on the composition. Their properties and phase transitions are being investigated. These copolymers are also strong candidates for electroactive applications. Emphasis of the presentation will be on key results and implications.

INTRODUCTION

Piezoelectric materials are widely used as active elements in stress gauges used to provide nanosecond, time-resolved stress measurements of rapid impulsive stress pulses produced by impact, explosion or rapid deposition of radiation. In the earliest work the gauges used crystalline sensors made of either x-cut quartz or various cuts of lithium niobate with thicknesses of many millimeters. The wave transit times through such sensors range from many tens of nanoseconds to a few microseconds. The upper response limits of the crystalline sensors are limited by either, or both, mechanical or electrical properties: dynamic yielding of the sensors or dielectric breakdown due to the large internal fields produced by the piezoelectric effect.

Although piezoelectricity in polyvinylidene fluoride (PVDF) was discovered by Kawai in 1969 [1] and piezoelectricity and ferroelectricity subsequently confirmed by Kepler in 1978 [2],
commercially available PVDF materials did not exhibit reproducible properties due to the critical importance of mechanical and electrical processing history. Early work by Bauer [3], which explored the behavior of polyvinylidene fluoride (PVDF) for high pressure applications, led to recognition of the need for such highly reproducible properties for PVDF. An international cooperative study between Institut Franco-Allemand de Recherches de Saint-Louis (ISL) and Sandia National Laboratories to develop the PVDF gauge, has shown that 25 µm thick PVDF film can be reliably used in a wide range of precise stress and stress-rate measurements [3]. Reliable behavior under the various extreme shock conditions requires specific sample preparations according to the Bauer process [4,6]. The 25-micron thickness of such PVDF sensors permits the gauges to be placed unobtrusively in a variety of locations within samples. Their direct stress-derivative or stress-rate signals of a few nanoseconds duration, and higher operating stress limits, provide capabilities not available with any other technique. The 10 nanoseconds transit time of a wave in PVDF achieves conditions in which the electrical behavior is described in the “thin mode”. That is, the electrical effects as the wave propagates within the sensor are not resolved to first order.

Historically, the introduction of gauges with direct measures of stress pulse characteristics at higher derivatives such as stress, Manganin, quartz, etc or particle velocity, velocity interferometer technique (VISAR), has led to qualitative improvements to model behavior of materials under the high-pressure, short duration conditions common in shock-compression loading conditions.

The capability of PVDF to provide a direct measure of rate-of-change of stress moves experimental capability to a new sensitivity. Recognizing the need for a reproducible material for the destructive conditions of shock compression, we have developed a new poling method [4] to process PVDF so that its physical properties exhibit a reproducibility approaching that of piezoelectric single crystals. Thus, the combination of precise conditions concerning highly reproducible samples provides an opportunity to describe the piezoelectric response of PVDF to high-pressure shock compression and large volume compression.

The behavior of PVDF has been studied over a wide range of pressures using high-pressure shock loading and has yielded well-behaved reproducible data for pressures up to 25 GPa in inert materials. In theses impact experiments between 0 and 12 GPa, identical impactor and sample materials (sapphire, quartz, Kel-F and Cu) were used to determine the PVDF piezoelectric response. Analysis of the shock-induced polarization response for 1 and 9 mm² precisely poled PVDF gauges in the “thin mode regime” using a Lagrangian hydrocode is recalled.

But, over 12 GPa, only Cu impactor and sample materials were used. These observations raise naturally the question of the loading path dependence of the piezoelectric response of PVDF at such higher shock pressure levels. Furthermore, shock-induced polarization or electrical charge can be released inside the shock-compressed impactor or sample materials. Also, studies of the piezoelectric behavior of PVDF gauges shielded in a new manner, has been recently conducted under impact loading using a two-stage light gas gun up to 35 GPa. Symmetric impact as well as non symmetric impact techniques on PVDF gauges are presented.

PVDF gauges have recently been utilized successfully for Hugoniot measurements of porous explosives. It is also shown that the shielding technique can be applied to shock pressure profile measurements “in situ” porous H.E. in a detonation regime. The measured shock pressure profiles with the PVDF gauge show a fast superpressure of a few nanoseconds followed by a pressure release down to a plateau level and then by a pressure decay.
P(VDF-TrFE) copolymers exhibit also unique piezoelectric properties over a wide range of temperature depending on the composition [7]. Their properties and phase transitions are briefly presented.

POLARIZATION TECHNIQUE

In the preparation of piezoelectric polymers and copolymers it is in general necessary to apply a high poling electric field to an essentially insulating material. The earliest electrical and most widely available process applied to pole PVDF films is the room temperature, ”Corona poling” method, which can produce large area, films for nominal applications which do not require high electrical quality. In such a large volume production method, quality and reproducibility is not desired.

For applications and materials studies requiring high quality and reproducibility, individual samples must be produced with well defined electrical properties in a process, which can control amplitude, duration and history of the electric field. With control of electrical field applied to an individual sample, electrical displacement, displacement current, remanent polarization, and homogeneity of polarization can be controlled. The ISL poling equipment, as shown in figure 1, allows us to adjust, in real time via a high voltage and data acquisition computer controlled system, the predetermined remanent polarization as well as the maximum displacement current measured at the coercive field for an individual PVDF gauge [3,4]. Further, with appropriate attention of the history of each sample, space charge in the samples can be eliminated [5]. With the Bauer cyclic poling process, reproducible remanent polarizations as large as 9 microcoulomb per cm² are routinely achieved in commercial processes. Because electric fields as high 5 MV per cm are utilized, inferior film is eliminated in the process. A typical PVDF sample response in the cyclic poling process is shown in figure 2. In the figure 2 both polarization and displacement are shown at various stages of the process. Starting at low electric fields, the sample is cycled through many ”loops” until a consistent behavior is indicated. Higher applied fields are then utilized until the desired stable polarization is achieved. A higher degree of reproducibility is achieved when the maximum displacement current at the coercive field is stabilized.

Figure 1. Poling process equipment.

Figure 2. Histories of hysteresis loops on a 25 µm thick biaxially stretched PVDF sample with a 1 mm² area. Typical displacement current and polarization versus voltage applied.
Each PVDF gauge [3], fabricated in this process is characterized with an individual poling history with well-defined electrical properties, better than 2%, which can be reproduced at will.

**PIEZOELECTRIC PVDF SHOCK RESPONSE**

**Experimental Arrangements**

The impact of a precisely controlled impactor mounted on a projectile upon a sample provides the most accurate and well-defined pressure achievable with any technique. In the impact experiment the symmetry conditions for identical impactor and sample materials require that precisely one half of the velocity at impact be imparted to the sample. With appropriate attention to detail, the velocity at impact can be determined to an accuracy and precision of 0.5%. The pressure resulting from the velocity imparted to the sample is the product of the velocity, the density and wave speed. With the use of single crystal materials of high elastic limits, pressures can be routinely achieved up to about 10 GPa with uncertainties of about 1%. This accuracy is significantly less than that which can be achieved with static pressure techniques. The time scale of the event is controlled by stress waves, which typically propagate through a PVDF sample in times of about 10 nanoseconds. The short duration of the loading creates conditions in which no heat is exchanged. Under this "Hugoniot" condition, the mechanical work results in specific internal energy, which raises [3] the sample temperature 10 to 1,000 °C.

The overall features of the precise impact loading techniques are shown in figure 3. A range of impact velocities from 250 m/s to 1.8 km/s is achieved with a powder gun to accelerate the projectile [3] to a preselected velocity. A range of impact velocities from 0.85 km/s to 3 km/s is achieved with a two-stage light gas gun. Planarity control, accuracy of velocities (0.5%), are comparable to those of our powder gun. Planar loading over the surface of the sample must be achieved in times short compared to the many nanosecond duration of the shock event. In the

**Figure 3.** The piezoelectric response of PVDF film is studied with the impact of standard materials with samples placed on the impact surface of the target. This experiment achieves the most precise high pressure loading of any technique, static or shock. Other “ramp-wave” loading is achieved by placing samples behind disks of fused quartz or "pyroceram".

EE2.3.4
powder gun experiments, PVDF gauges are placed on the impact surface of either z-cut quartz, sapphire crystals or selected copper which serve as standard materials to define the stress. This technique can achieve pressures from 2 to 25 GPa. For lower pressures, a modification of the technique, which provides «ramp» increases in pressure in time, uses fused quartz. The polymer material Kel-F can also be used as a standard material, but its properties are complicated due to viscoelastic responses (loading history).

With the two-stage light gas gun, symmetric impact as well as non-symmetric impact and reverse impact techniques [8] on PVDF gauges are used in order to study the influence of the loading path at shock pressures higher than 12 GPa.

Since signal rise times are typically a few nanoseconds, low inductance, GHz instrumentation is utilized throughout. At present Tektronix TDS 684B digitizers are found to provide the best signal recording capability. The accuracy of such digital recording is a few percent. PVDF sample responses are determined by recording the short-circuit current during the time the shock waves are reverberating within the samples. The electrical charge is determined by numerical integration of the recorded current. Typically, the current is recorded on two independent digitizers of different sensitivities to broaden the dynamic range of the recording.

RESULTS UNTIL 25 GPa: LAGRANGIAN ANALYSIS

The piezoelectric charge associated with a particular peak pressure is observed upon integration of the current pulse. The charge data are observed to be a continuous function of the shock pressure until 25 GPa. As reported in [4], it should be recalled here that the experimental electrical charge Q released by the piezoelectric PVDF film can be correlated with the global one-dimensional true strain, \( \varepsilon \), of PVDF. The following relationships have been found to fit well the dependence of the electrical charge Q versus true strain \( \varepsilon \):

\[
\begin{align*}
Q & = 1.88 \cdot \ln (1 + 10. \varepsilon) + 0.0047; \\
Q & = 12.16 \cdot \varepsilon + 0.16; \\
\end{align*}
\]

where \( \varepsilon = \ln \left(\frac{v(t)}{v(t_0)}\right) \), \( v = \) PVDF specific volume and \( t = \) time.

The piezoelectric charge released Q is a nonlinear function of the true strain \( \varepsilon \), in the true strain values region (0 - 0.03), and is a linear function of the true strain \( \varepsilon \), in the range (0.03 - 0.45), figure 4. By introducing the experimental relations (1) and (2) into the hydrocode DYNA (Livermore-Software Two Dimensional Hydrodynamic Finite Element Code) or SHYLAC (Hydrodynamic Lagrangian Simulation of Shocks) [4], we can compute the theoretical current or charge profile for a given test. The calculation allows us to determine the stress as well. Figure 5 shows, for both 1 mm\(^2\) and 9 mm\(^2\) PVDF gauges, the piezoelectric response versus stress, based on experimental and computed data. We observe, figure 5, that the experimental and computed charges versus stress are in very good agreement with the published data (0 - 10 GPa) of R. A. Graham [6] on our PVDF gauges. The piezoelectric response appears to be independent of the loading path below 12 GPa. As shown in the same figure 5, the piezoelectric response based on experimental and computed data has been determined until 25 GPa.
For the experiments above 12 GPa, symmetric impact in using copper for both projectile and target were used. The behavior indicates a strongly nonlinear character.

PVDF RESPONSE UNDER TWO-STAGE LIGHT GAS GUN IMPACT LOADING: EXPERIMENTS AND RESULTS

High pressure piezoelectric response of 1 mm² PVDF gauges under impact loading using a two-stage light gas gun up to 35 GPa has been studied. For varying the loading path, symmetric impact as well as non symmetric impact and reverse impact techniques on PVDF gauges have been used [8].

Non Symmetric Impact Experiments

Viscoelastic behaviors are strongly manifested in polymeric solids. It should be borne in mind that shock-induced polarizations [6] are widely observed in polymeric materials, above threshold compression of about 15%. Shock measurements with PVDF placed on the impact surface of polar materials, i.e. polymers, without paying attention to the electrical environment due to the induced polarization, have led to an anomalous response [4]. In the non-symmetric impact experiment, 3 mm thick Aluminum (Al 2024) or 2 mm thick OFHC copper sample were mounted on projectile The target consisted of a 10 mm thick electrically shielded Kel-F polymer. The electrical shielding was achieved via a deposition of thin metallic layers sputtered on the polymer sample and then connected to the ground material. This leads us to avoid the capacitive coupling of PVDF with the environment. The PVDF gauge sandwiched between a 125 μm thick film and a 25 μm thick film of PFA –Teflon is bonded on the Kel-F target. A typical record of the piezoelectric charge versus time obtained in such experiments is depicted in figure 6. As we can see on the figure 6, the negative jump of the electrical charge, which corresponds, to the early shock is followed by a rapid decrease of the charge corresponding to a rapid relaxation to higher velocities. Then, the charge continues to decrease with a slope corresponding to a slow

Figure 4. Electrical charge versus the computed strain $\varepsilon$.

Figure 5. The electrical charge observed at various peak pressures is shown for PVDF. The experimental and computed data are on the same curve.
relaxation to higher velocities [6] until the release wave from the impactor comes. Looking at the Kel-F relaxation, we cannot attain in our experiment the stress equilibrium, and consequently the charge released cannot be correlated with the induced stress.

**Reverse Impact Technique**

The reversed impact configuration [8] consists of the inverse of the above described experiment. Projectiles are made of Kel-F polymer shielded in the same manner as described above. PVDF gauges are bonded on sapphire or Al or Cu targets, figure 3. In a first series of experiences, single crystals of z-cut sapphire which are elastic to stresses in excess of 14 GPa were used as the target. In both cases, figure 7, a plateau follows the early shock. In the case of the PVDF embedded between two pieces of 1 and 2 mm thick sapphire, the equilibrium is reached after 0.10 μs. For the test with the PVDF bonded between a 125 μm thick PFA-Teflon and a 3 mm thick sapphire, we can observe after 0.15 μs a small change in the charge. At a time of 0.52 μs, the change in the shape of the charge is due to the arrival of the released wave coming from the 3 mm thick sapphire backer. At this time, the leads of the PVDF gauge are destroyed. In both cases, the piezoelectric charge can be correlated with the induced stress. In a second series of experiments, shielded Kel-F projectiles impacted PVDF bonded on a Cu target. The PVDF gauge was sandwiched between two 125 μm thick films of PFA-Teflon. Figure 8 gives a typical record of the piezoelectric charge released. The equilibrium is reached after two compression steps. Even a small relaxation is observed, the charge can be correlated with the equilibrium-induced stress.

**Symmetric Impact Technique**

Impactor and sample materials are identical. One half of the velocity at impact is imparted to the sample. Figure 9 shows the piezoelectric response of the PVDF gauge subjected to the impact of a Cu projectile at a velocity of 1588 m/s. The loading of the film proceeds as a series of reverberations with increasing stress until equilibrium is reached. The charge is correlated with the equilibrium stress (for example, figure 9 at 0.25 μs).

**Figure 6.** The figure shows the electrical charge released from shock-compressed PVDF bonded on a Kel-F polymer. The Al impactor velocity is equal to 2958 m/s.

**Figure 7.** The continuous curve corresponds to the PVDF bonded on a 3 mm thick sapphire. The dotted curve corresponds to the PVDF bonded inside two pieces of 1 and 2 mm thick sapphire.
RESULTS UNTIL 35 GPa : LOADING PATH DEPENDENCE

Table 1 recapitulates the results obtained for reliable experiments.

<table>
<thead>
<tr>
<th>Type of experiment</th>
<th>Impact velocity (m/s)</th>
<th>Stress (GPa)</th>
<th>Charge (µC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kel-F→Sa</td>
<td>1624</td>
<td>12.2</td>
<td>4.26</td>
</tr>
<tr>
<td>Kel-F→Sa</td>
<td>1850</td>
<td>14.7</td>
<td>4.79</td>
</tr>
<tr>
<td>Kel-F→Al</td>
<td>2695</td>
<td>17.8</td>
<td>4.89</td>
</tr>
<tr>
<td>Kel-F→Cu</td>
<td>2561</td>
<td>22.9</td>
<td>5.75</td>
</tr>
<tr>
<td>Cu→Cu</td>
<td>1357</td>
<td>30.0</td>
<td>6.16</td>
</tr>
<tr>
<td>Cu→Cu</td>
<td>1588</td>
<td>36.3</td>
<td>6.50</td>
</tr>
</tbody>
</table>

Figure 10 shows the experimental and computed charges versus stress including these results. The observed charge versus stress data for these various loading paths show that the final charge seems to be independent of the loading path.

Figure 8. The figure shows the electrical charge released from shock-compressed PVDF bonded on a Cu target. The Kel-F impactor velocity is equal to 2561 m/s.

Figure 9. The electrical charge versus time is given for a Cu symmetric impact on PVDF. The projectile velocity is equal to 1588 m/s.

Figure 10. The electrical charge observed at various loading path pressures is shown for PVDF.
PVDF gauges have recently been utilized successfully for Hugoniot measurements of porous explosives [4]. Figure 11 gives the sketch of the experimental arrangement used for Hugoniot measurements. After many trials, we have been able to shield the explosive as described in the preceding section. Sputtering of 0.01 µm thick Pt and 0.1 µm thick Au layers could be achieved on a high explosive (Formex) available at ISL.

This H.E. (Formex) contains 89% PETN and 11% rubber. The average density of this porous explosive is equal to 1.35 g/cm³. Measurements, figure 12, of shock pressure profiles and shock velocities (deduced from H.E. thickness over transit time) have led to the Hugoniot determination at low input shock compression. The input wave profile, given by the PVDF gauge placed between the copper disk and the explosive figure 12, seems to follow a shock profile similar to that observed by Anderson on porous materials [8]. But at the moment there is no clear explanation for the pressure collapse observed just after the first pressure jump. Nevertheless, it has been observed that the shape of the shock input influences the H.E. reaction.

Figure 11. Experimental arrangement for Hugoniot measurements of the porous HE “Formex”.

Figure 12. The dotted curves correspond to the PVDF pressure profiles obtained on H.E. sandwiched between an aluminum 2024 disk and a PMMA disk. The continuous curves correspond to the PVDF pressure profiles obtained on H.E. sandwiched between a copper disk and a PMMA disk.
SHOCK PRESSURE PROFILES OBTAINED WITH PVDF GAUGES IN SITU POROUS H.E. IN A DETONATION REGIME

The overall features of H.E. studies under precise impact loading are shown in figure 13. On the H.E. Formex samples, in the 12.12.5 mm³ parallelepiped form, the same shielding technique is applied.

Figure 13. Experimental arrangement for H.E. pressure measurements.

As indicated on figure 13, a PVDF gauge of 1 mm² in active area is placed between the copper plate and the first H.E. sample, then another PVDF gauge is bonded between the two H.E. samples and finally the last PVDF gauge is mounted between the second H.E. sample and a shielded piece of Kel-F. The PVDF gauges also have to be bonded between two 25 µm thick films of PFA-Teflon. Impact velocities were chosen equal to 650 m/s. Due to the symmetric precise impact, planar loading over the surface of the 1.5 mm thick copper plate is achieved. Then the input shock wave is transmitted to the explosive. The input stress loading in Formex is of the order of 2.5 GPa, which is high enough to induce the detonation at a depth of about 0.5 mm. The detonation wave propagates through the explosive and is transmitted to the Kel-F backing which is perfectly matched to the PVDF gauge. In order to verify in such an experiment the reliability of the shielding, when the detonation wave occurs [9], we have placed the three gauges in the -/+ electric orientation during a test. The same experiment has been repeated with PVDF gauges placed in the +/- orientation, which is the usual orientation utilized [3]. The electrical signals from the PVDF gauges show the same shape in current and in electrical charge as well as in amplitude for both experiments. Typical record of reduced data for the first PVDF gauge in shock pressure versus time is depicted on figure 14. After a shock pressure jump and a plateau, a slight collapse is observed, then the pressure, following the reaction of the H.E., increases up to a maximum value of 9.7 GPa. Figure 15 shows the pressure versus time for the second PVDF gauge embedded in situ the H.E. The PVDF shock pressure profile shows a fast superpressure of a few nanoseconds duration at a level of 14.5 GPa, followed by a pressure release down to a plateau at a pressure level of about 10.5 GPa and then a pressure decay [11]. The pressure plateau figure 15, measured at 10.5 GPa is in agreement with the C.J. pressure data measured and computed for close PETN compositions and published by H.C. Hornig et al [10].
P(VDF$_{1-X}$-TrFE$_X$) COPOLYMERS

P(VDF-TrFE) copolymers [7] exhibit tailorable ferroelectric, piezoelectric and structural properties that may be superior to those of PVDF for some shock gauge applications. Consequently, we have been investigating these properties as functions of static and dynamic pressure. The phase diagram for P(VDF$_{0.77}$ TrFE$_{0.23}$) was determined from dielectric spectroscopy measurements as functions of temperature, hydrostatic pressure and frequency following established procedures [7]. The important features in the phase space for PVDF and its copolymers are (with increasing temperature) a prominent molecular relaxation process centered around T$_\beta$=270K and the melting transition (T$_m$). In addition the copolymers exhibit a ferroelectric transition (T$_c$) below T$_m$. All of these transitions have strong influences on the
electrical and mechanical responses of these polymers. The transitions at $T_\beta$, $T_C$, and $T_m$ are well-defined features in the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the dielectric response, figure 16. All of these features shift to higher temperatures with increasing pressure, as shown. In figure 17, the initial slopes of the phase boundaries $dT_x/dP$ for $T_\beta$, $T_C$ and $T_m$ are $11\pm1$ (independent of frequency), $24\pm1$ and $41\pm1$ K/kbar, respectively. The slope $dT_\beta/dP$ is the same as for PVDF. The slopes $dT_C/dP$ and $dT_m/dP$, exhibit strong dependence on composition [7]. Specifically and for comparison, $dT_C/dP = 30\pm2$K/kbar for P(VDF$_{0.70}$ TrFE$_{0.30}$) and $dT_m/dP=29\pm2$K/kbar for PVDF and $53.4$K/kbar for P(VDF$_{0.70}$ TrFE$_{0.30}$). The melting curve of PVDF is the dashed curve, figure 17.

CONCLUSION

The present work provides the description of piezoelectricity in PVDF at very high pressure. The piezoelectric response for both precisely 1 mm$^2$ and 9 mm$^2$ PVDF gauges subjected to shock loading is observed to be identical. The electrical output of the gauge is determined solely by the piezoelectric response, i.e. there is essentially no domain switching. Studies of the piezoelectric behavior of PVDF gauges under impact loading using a powder gun and a two-stage light gas gun have been presented. In spite of the difficulties encountered to obtain reliable measurements, the valid data obtained show the reproducible response of our ISL PVDF independently of the loading path until 35 GPa. PVDF gauges in a low-inductance configuration can measure detonation waves of some specific porous H.E. It is also shown for PVDF and P(VDF-TrFE) copolymers that pressure strongly stabilizes the ferroelectric phase.

REFERENCES