SAN097-2282C
SAND--97-2282C
CONF-970707--13

ADVANCES IN FERROELECTRIC POLYMERS FOR SHOCK COMPRESSION SENSORS

F. Bauer*, H. Moulard*, G. Samara**

* *Institut Franco-Allemand de Recherches, (ISL), Saint-Louis, France*
** *Sandia National Laboratories, Albuquerque, NM 87185 USA*

Our studies of the shock compression response of PVDF polymer are continuing in order to understand the physical properties under shock loading and to develop high fidelity, reproducible, time-resolved dynamic stress gauges. New PVDF technology, new electrode configurations and piezoelectric analysis have resulted in enhanced precision gauges. Our new standard gauges have a precision of better than 1% in electrical charge release under shock up to 15 GPa. The piezoelectric response of shock compressed PVDF gauges 1 mm^2 in active area has been studied and yielded well-behaved reproducible data up to 20 GPa. Analysis of the response of these gauges in the " thin mode regime " using a Lagrangian hydrocode will be presented. 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. Emphasis of the presentation will be on key results and implications.

INTRODUCTION

Although ferroelectricity and piezoelectricity in Polyvinylidene Fluoride were discovered by Kawai (1) in 1969 and subsequently confirmed by Kepler (2), the materials commercially available did not exhibit reproducible properties due to the critical importance of mechanical and electrical processing history. Subsequently, the mechanical and electrical processes needed to achieve precisely known and reproducible electrical properties were developed (3).

The availability of reproducible samples provides an opportunity to study the materials and to describe the piezoelectric response of PVDF under the destructive, very high pressure conditions achieved in controlled shock loading (4). Previous work (3) has shown that selected and precisely poled standard 9 mm^2 PVDF gauges could respond precisely to pressures of 25 GPa. For 1 mm^2 gauges, at pressures up to 12 GPa, well-defined signals are observed. But the usefulness of 1 mm^2 PVDF gauges was hampered by observations of differences in responses even at low shock pressure.

The need to develop high fidelity, reproducible time-resolved dynamic stress gauges especially with small active areas, has led us to continue these studies of shock compression response of PVDF polymers, and to understand the physical properties under shock loading. The present paper will briefly summarize the advances in new poling technology, as well as the development of high fidelity, reproducible, time-resolved dynamic stress gauges with small areas. The shock induced polarization for 1 and 9 mm^2 precisely poled gauges are

DISCLAIMER

compared. The analysis of the response of these gauges and of standard PVDF gauges in the " thin mode regime " using a Lagrangian hydrocode has been revisited. Effects of pressure on the dielectric properties of P(VDF-TrFE) copolymers have been also investigated and will be summarized.

PROGRESS IN TECHNOLOGY

In order to enhance the precision of the gauges and to avoid some deviations in the gauge response as reported before (3), we have developed new poling equipment. This equipment 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 to an individual sample. Further, with appropriate attention to the history of each sample, space charge in the samples can be eliminated (3), (4). A higher degree of reproducibility is achieved when the maximum displacement current at the coercive field is stabilized. Each sample 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.

HIGH PRESSURE APPARATUS: PRECISE IMPACT LOADING

In the impact experiment the symmetry conditions for identical impactor and sample materials require that precisely one-half the velocity at impact be imparted to the sample. In the electrical measurement circuit the expensive CVR is replaced by a CMS resistance. Sample response is determined by recording the short-circuited current during the time the shock waves are reverberating within the samples until mechanical equilibrium is achieved corresponding to the longitudinal stress in the standard material. The electrical charge is determined by numerical integration of the recorded current. A range of impact velocities from 0.25 km/s to 1.8 km/s are achieved with a powder gun which accelerates the projectile to a preselected velocity. PVDF samples are placed on the impact surface of either z-cut quartz, sapphire crystals or selected copper which serve as the standard materials to define the stress. Typical times to achieve equilibrium in the 25 micron films are 50 to 150 nanoseconds

PIEZOELECTRIC POLARIZATION AT PRESSURE

Figure 1 shows the results of experiments to peak pressures of about 12 GPa for both 1 mm^2 and 9 mm^2 PVDF gauges. Data are shown for standard materials as well as those with the copper, the fused quartz ramp loading or KelF impactors. Data for 1 mm^2 PVDF including " Barker pillow " isentropic loading (where the stress is measured simultaneously with a 9 mm^2 PVDF) are also shown on the same Figure 1.

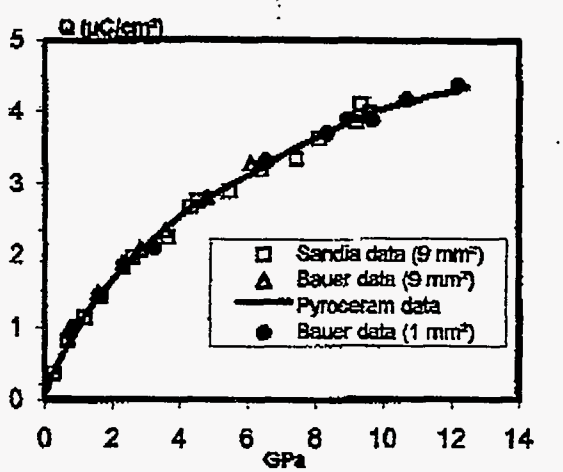

FIGURE 1. Observed charge vs stress data for the various loading paths show that the final charge is independent of path. At low stress the continuous response data is compared to shock response (3), (4).

The deviation of experimental points about their representative values is thought to be within the experimental uncertainty of the recording instruments and less than 1% in electrical charge release. The behavior indicates a strongly non-linear character. The shock induced polarization for both precisely poled gauges under shock loading is observed to be identical. The expe-

rimental results are in excellent agreement with the Graham-Sandia data (4), and recalled here.

LAGRANGIAN ANALYSIS

Even though the piezoelectric polarization is observed to be continuously nonlinear with stress (3), the observed polarization with the computed true strain of PVDF is non linear in the true strain values region (0 - 0.03), and appears to be approximately linear in the range (0.03 - 0.45). Figure 2 gives the electrical charge versus true strain for both ISL and Sandia data (3)

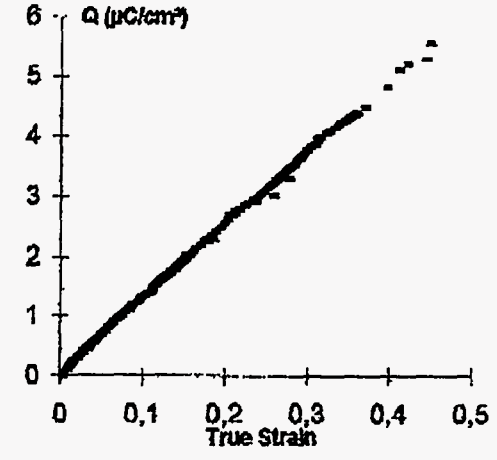

FIGURE 2. Electrical charge vs the computed true strain ε.

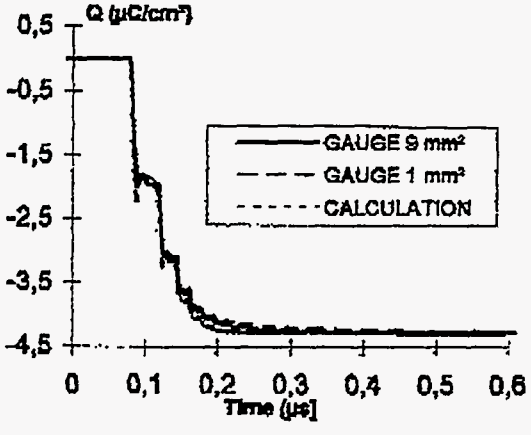

FIGURE 3. Comparison between experimental and computed data.

In introducing (5) the experimental (Q-ε) relation into the hydrocode DYNA or SHYLAC, we can compute the theoretical current or charge profile for a given test. Figure 3 shows the computation-experiment comparisons for both 1 mm^2 and 9 mm^2 PVDF gauges in the same symmetric copper impact test (shock pressure : 12 GPa). The calculation allows us to determine the stress too. We observe that the experimental and computed charge versus stress are in very good agreement with the published data (0 - 10 GPa) of R. A. Graham (4) on our PVDF gauges, Figure 4.

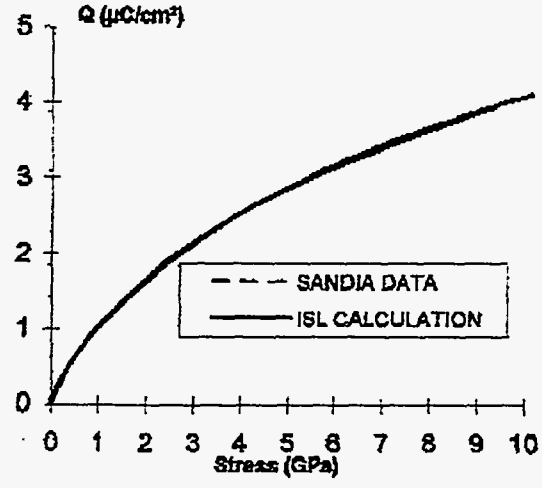

FIGURE 4. Experimental and computed charge vs stress.

P (VDF_{1-X}-$TRFE_X$) COPOLYMERS

P(VDF-TrFE) copolymers (6) 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 (6). The important features in the phase space for PVDF and its copolymers are (with increasing temperature) a prominent molecular relaxation process centered around

T_β=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 transition at T_β, T_C, and T_m are well-defined features in the real (ε') and imaginary (ε") parts of the dielectric response, Figure 5. All of these features shift to higher temperatures with increasing pressure, as shown.

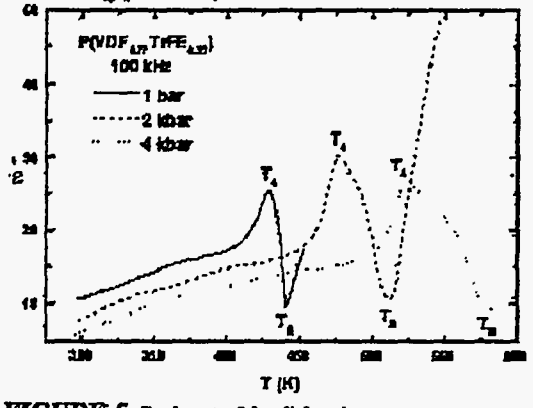

FIGURE 5. Real part of the dielectric constant vs temperature showing the large influence of pressure on the various phase transitions in the copolymer.

In Figure 6, the initial slopes of the phase boundaries dT_x/dP for T_β, T_C and T_m are 11±1 (independent of frequency), 24±1 and 41±1 K/kbar, respectively. The slope dT_β/dP is the same as for PVDF. The slopes dT_C/dP and dT_m/dP, exhibit strong dependence on composition (6). Specifically and for comparison, dT_C/dP = 30±2K/kbar for $P(VDF_{0.70}\ TrFE_{0.30})$ and dT_m/dP=29±2K/kbar for PVDF and 53.4K/kbar for $P(VDF_{0.70}\ TrFE_{0.30}$. The melting curve of PVDF is the dashed curve, Fig. 6.

CONCLUSION

Advances in poling process of 1 mm^2 and 9 mm^2 PVDF gauges have been achieved. The shock induced polarization for both precisely poled gauges sustained to shock loading greater than 12 GPa is observed to be identical. Computed data via numerical analysis are in good agreement with the experimental and published data. It is clear (6) that pressure strongly stabilizes the ferroelectric phase. The electrical output of the gauge is determined solely by the piezoelectric response, i.e., there is essentially no domain switching. The much larger T_m(P) slope suggests that the copolymer may have advantages over PVDF for high pressure (>100kbar) applications. Shock experiments should be designed to avoid or take the strong relaxational response into consideration.

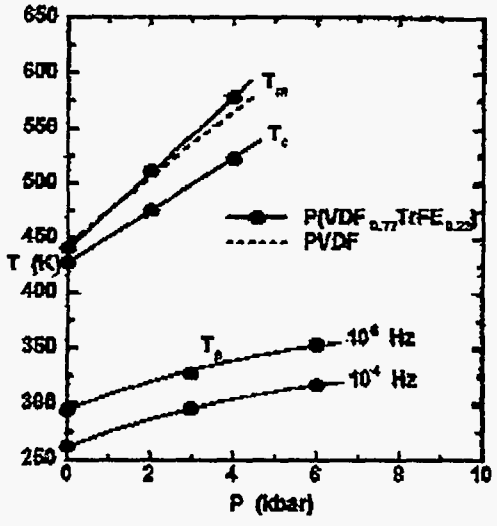

FIGURE 6. The Temperature Pressure phase diagram for $P(VDF_{0.77}TrFE_{0.23})$.

ACKNOWLEDGMENTS

This work in ISL was supported by the DRET under Contract and in Sandia by the United States Department of Energy under Contract DE-AC04-94AL85000. We express our appreciation to I.S.L. and Sandia staffs.

REFERENCES

1. H. Kawai, *J. Appl. Phys.* 8, pp 975, (1969).
2. R.G. Kepler, *Ann. Rev. Phys. Chem.* 29, 497 (1978).
3. F. Bauer and R.A. Graham, *Ferroelectrics*, 171, 95 (1995) and references therein.
4. R.A. Graham, *Solids under High Pressure Shock Compression*, New York: Springer Verlag, 1993, pp 103-113.
5. H.Moulard, F.Bauer, *Proceedings of Shock Waves in Condensed Matter*, North-Holland, pp 1065-1068, 1995
6. G. A. Samara and F. Bauer, *Ferroelectrics*, 135, 385 (1992) and references therein.