PIEZOELECTRIC AND PYROELECTRIC PROPERTIES OF POLY(VINYLDENE FLUORIDE)
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PIEZOELECTRIC AND PYROELECTRIC PROPERTIES OF POLY(VINYLIDENE FLUORIDE) FILMS AT HIGH HYDROSTATIC PRESSURE

by

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Abstract

The pressure dependence of the piezoelectric hydrostatic pressure coefficient, \( d_p \), and the pyroelectric coefficient, \( \gamma_p \), was determined from atmospheric pressure to 7 Kbar over a temperature range from \(-80^\circ C\) to \(+48^\circ C\) for poled, uniaxially oriented film. The effect of the glass transition on \( d_p \) and \( \gamma_p \) as a function of pressure is compared to the pressure dependence of the glass transition temperature obtained from dielectric studies. The ratio of \( d_p/\gamma_p \) as a function of pressure and temperature is presented.
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Introduction

Many recent investigations have been concerned with the origin of the piezoelectric and pyroelectric properties of poled poly(vinylidene fluoride) (PVF$_2$) films. Various mechanisms for the observed phenomena have been suggested, including bulk polarization due to switching of molecular dipoles in the polar crystals,\cite{1,2} non-uniform charge injection leading to asymmetric distribution of real charge in the film,\cite{3} field induced charge trapping of injected charge or ionic charges present as impurities.\cite{4} Other suggestions such as a reversible temperature dependence of the crystallinity\cite{5} and metal-polymer interfacial phenomena\cite{6} have been proposed as possible contributing mechanisms.

A detailed theoretical model proposed by Broadhurst\cite{7} et al, assumes that PVF$_2$ crystals are ferroelectric and that the direction of polarization of polar crystallites can be changed by field. Thus, poling produces a remnant polarization, $P_0$, which changes as a result of changes in temperature (pyroelectricity) or applied stress (piezoelectricity). Although it is now established that this theory can account largely for the observed phenomenon, it is possible that other mechanisms may play a role in certain cases. PVF$_2$ is known to be a semicrystalline polymer consisting of lamellar crystals in an amorphous matrix. Further studies are required in order to gain further insight into the relationship between structure and morphology and the electrical properties. R. G. Kepler and R. A. Anderson\cite{8} were able to account for only one-half of the total pyroelectricity on the basis of secondary pyroelectricity. They were unable to detect any
appreciable contribution from primary pyroelectricity and suggested that a large contribution arose from a reversible temperature dependence of the crystallinity.\textsuperscript{7} Other suggested mechanisms may also be important. In order to clarify these problems data is needed across a wide range of temperature and pressure. Of particular interest is the effect of the glass transition temperature $T_g$.

No studies have been made at high pressures and only a few investigations have been made over a wide enough temperature range to include the $T_g$. Buchman\textsuperscript{2} found a decrease in the pyroelectric effect with increasing temperature for PVF$_2$ in the glassy state, while Burkard and Pfister\textsuperscript{9} observed a small increase which they related to the glass thermal expansion. The latter observers also noticed a small discontinuity in slope for the pyroelectric coefficient at $T = +20^\circ$C. Ohigashi\textsuperscript{10} determined the variation of several piezoelectric constants ($d_{33}$, $e_{33}$, $d_{31}$, $e_{31}$, $d_{32}$, $e_{32}$) with temperature from $-170^\circ$C to $+100^\circ$C at high frequencies, 20KH$_z$ to 30MH$_z$. Furukawa, Aiba and Fukada\textsuperscript{11} determined the variation of both real and imaginary components of $e_{31}$ with temperature from $-150^\circ$C to $+100^\circ$C at 10H$_z$. In both studies an increase in $e_{31}$ to a maximum value followed by a decrease was observed. The temperature at which the maximum occurred differed by $\approx 80^\circ$C in the two studies probably because of the difference in frequencies used.

A comparison of piezoelectricity and pyroelectricity over a large range of temperature and pressure provides an indication of whether both phenomena originate from a common source. The pyroelectric constant $P_y$ can be defined:

$$P_y = \left. \frac{d(Q/A)}{dT} \right|_{E = 0}$$

where $\frac{d(Q/A)}{dT}$ is the rate of change of surface charge density with temperature. The hydrostatic pressure coefficient can be defined

$$d_p = \left. \frac{d(Q/A)}{dP} \right|_{E = 0}$$
where \( \frac{d(Q/A)}{dP} \) is the rate of change of surface charge density with pressure. If \( \frac{d(Q/A)}{dT} \) and \( \frac{d(Q/A)}{dP} \) only originate from dimensional changes we have

\[
P_y = \left(\frac{\alpha}{s}\right) d_p
\]

where \( \alpha \) is thermal expansion coefficient and \( s \) is the compliance.

We have determined \( d_p \) and \( P_y \) at pressures up to 7.0 Kbar and in a temperature range from \(-80^\circ C\) to \(+48^\circ C\). The pressure and temperature dependence of \( P_y \) has been reported elsewhere\(^{12}\) but are presented again here to provide a good comparison with the piezoelectric data.

**Experimental**

Poled, uniaxially oriented PVF\(_2\) films (piezofilm - obtained from Kureha Company) were used. Piezoelectric, pyroelectric and other physical properties of the film are listed in Table 1. X-ray diffraction photographs showed that the crystal structure was phase I and that the film was highly oriented (C-axis in the draw direction.

The high pressure electrical call is described in a separate publication.\(^{12}\) It consists of a thick-walled cylinder which could be pressurized up to 7.0 Kbar and contained an internal heater which, used in conjunction with external cooling using liquid nitrogen, permitted excellent temperature stability and controlled heating and cooling down to \(-196^\circ C\).

In the measurement of the hydrostatic piezoelectric coefficient \( d_p \), the same procedure was used at all temperatures and pressures. The sample was first heated to the required temperature \( (T_0) \) and then pressurized to a constant pressure \( (P_0) \). The electrodes were then short-circuited at the new temperature and pressure until the sample was completely relaxed. The pressure was then increased slowly in 0.05 Kbar steps up to a pressure \( P = P_0 + 0.5 \) Kbar. The change in surface
charge $Q$ produced by the application of pressure was measured using an electrometer (Keithley model - 616) in the charge mode. We adopted an operational definition

$$d_p = \frac{1}{A_0} \left( \frac{\partial Q}{\partial P} \right)_{E = 0}$$

where $A_0$ is the initial area. In the plot of integrated charge $Q$ versus pressure, the initial slope at $P_0$ was used to determine $d_p$.

The same value for $d_p$ was found using either increasing or decreasing pressures. Since abrupt changes in pressure can introduce change in temperature (for a constant volume cell) small changes in polarization could arise from the pyroelectric effect. We determined the maximum error due to this effect to be $-3\%$.

The pyroelectric data reported here was obtained using the same electrical cell and varying temperature (as opposed to pressure). The experimental procedure is presented in a previous publication.\(^{12}\)

Since measurements were made over a wide range of pressure and temperature, the film could be in the glassy state either because of the low temperature or the high pressure. The pressure dependence of the glass transition temperature was determined by connecting the electrodes to a commercial device (Toyo Seiki Piezotron) and measuring the dielectric loss, $\varepsilon''$, at $3 \text{ Hz}$. The maximum in $\varepsilon''$ obtained by ramping temperature up and down through the glass transition region was assumed to correspond to $T_g$.

Results and Discussion

Fig. 1 shows the pressure dependence of $d_p$ at various temperatures from $-48^\circ\text{C}$ to $+48^\circ\text{C}$. $d_p$ decreases with increasing pressure at all temperatures, the most rapid decrease occurring at the lowest pressure and highest temperature. At room temperature the decrease is $\sim 25\%$ over the first 1 Kbar. The isotherm
at 24°C shows some discontinuity in slope at ~5.0 Kbar. This discontinuity is also evident in the lower temperature isotherms but shifted to lower pressures. We attributed this to the pressure induced glass transition \( P_g \), which at 24°C occurs at ~5 Kbar. For temperatures below ~48°C, \( d_p \) decreases smoothly with pressure, which would be expected since the polymer is in the glassy state over the entire range. At temperatures above 48°C, \( P_g \) is greater than 7.0 Kbars and so the variation of \( d_p \) with pressure is also smooth. It is interesting that the change is \( d_p \) as the pressure induces a change from the rubbery to the glassy state is so small. The pressure dependence of \( P_y \) showed a similar behavior and is shown in Fig. 2.

Fig. 3 shows the temperature dependence of \( d_p \) at various pressures up to 7.0 Kbars. For comparison, Fig. 4 shows the temperature dependence of \( P_y \) at various pressures. The immediate impression is that both \( d_p \) and \( P_y \) show the same general dependency. At atmospheric pressure, below ~55°C both \( d_p \) and \( P_y \) decrease slowly with increasing temperature; above this temperature both constants increase rapidly up to +48°C with some change of slope at ~20°C. The effect of pressure is to shift this general dependency to higher temperatures.

The minimum in \( d_p \) and \( P_y \) (observed at ~55°C) at atmospheric pressure is very close to the glass transition temperature for PVF₂. In Fig. 5 the pressure dependence of the glass transition temperature \( T_g (P) \) of the film is shown. This data was determined from the dielectric loss spectrum obtained at various pressures up to 7.0 Kbar. The temperature at which the minimum of \( d_p \) occurs is shown plotted on the same figure. The curves run closely parallel to each other suggesting similar origins. The constant difference in absolute temperature between the two curves is quite reasonable considering the difference in technique used. In fact the values obtained from \( d_p \) and \( P_y \) measurements are very close to values of \( T_g \) determined by dynamic mechanical\(^{13}\) and other tests.
The high temperature anomaly (-20°C at atmospheric pressure) is more pronounced at the highest pressures. The pressure dependence if the transition temperature (which we will call $T_c$) is less than that of $T_g$ and so at the highest pressures these two transitions approach each other.

The transition temperatures $T_g$ and $T_t$ divide the temperature dependence of $d_p$ and $p_y$ into three regions; below $T_g$, from $T_g$ to $T_t$, and above $T_t$. Below $T_g$, $p_y$ appears to decrease steadily with increasing temperature, while $d_p$ shows a shallow maximum with a slight decrease just before $T_g$. More recent measurements taken below -90°C. Buchman\textsuperscript{2} also observed a decrease in $p_y$ for PVF$_2$ in the glassy state although this was not observed by Burkard and Pfister.\textsuperscript{9} The decrease in $p_y$ is small, \sim 0.1 \text{nc/cm}^2 from -82°C to -48°C, but is observed at all pressures. We have no satisfactory explanation for this at the present time. Both thermal expansion, compressibility and the greater librational motion of chains at higher temperatures would lead to steady increases in $d_p$ and $p_y$ with temperature. Present theories of pyroelectricity and piezoelectricity appear unable to adequately explain the observed behavior of PVF$_2$ in the glassy state.

Between $T_g$ and $T_t$ both $d_p$ and $p_y$ increase rapidly at first and then level off as the temperature approaches $T_t$. At higher pressures this gives rise to a plateau region. A similar behavior was also observed by Burkard and Pfister although not by Buchman. Volumetric analysis of PVF$_2$ resin crystallized in the phase II form shows a $T_g$ at -52°C and another higher temperature relaxation at about 13°C.\textsuperscript{14-16} Dynamic mechanical tests also show a loss peak \sim 20°C.\textsuperscript{13} It has been suggested that this transition is related to morphological features.\textsuperscript{14} Further studies are required to clarify this phenomenon, but in any event the change in temperature dependence of both $p_y$ and $d_p$ appear to be related to this relaxation.
Figs. 6a and 6b show the ratio of $d_p/p_y$ at various high pressures and temperatures from -84°C to +48°C. Theoretical studies predict that the ratio should be \(-5.0 \times 10^{-3} \text{ cm}^2/\text{K/N}\). This is in agreement with results obtained at atmospheric pressure and temperature and implies that both $d_p$ and $p_y$ result only from dimensional changes or

$$p_y = \frac{a}{s} d_p$$

Figs. 6a and 6b show that the ratio varies with temperature and pressure from \(-3.0 \times 10^{-3} \text{ cm}^2/\text{K/N}\) to \(-9.0 \times 10^{-3} \text{ cm}^2/\text{K/N}\). Further experimental studies of $\alpha$ and $s$ are needed to determine their temperature and pressure dependence and these are being carried out at the present time. For pressures up to 2.0 Kbar, $d_p/p_y$ increases in absolute value with temperature in the glassy state. Above $T_g$ the ratio drops until $T_t$ is reached when it begins to increase again. At 3.0 Kbars a very rapid decrease in $d_p/p_y$ occurs at the glass transition from $8.9 \times 10^{-3}$ to $5.7 \times 10^{-3}$ as the temperature increases 12°C. At higher pressures $T_g$ and $T_t$ are too close to resolve individual responses. It is interesting to note that at the highest temperature, 48°C, the ratio $d_p/p_y$ varies only from $4.55 \times 10^{-3}$ to $5.05 \times 10^{-3}$ at all pressures.

Acknowledgment

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References

2. P. Buchman, Ferroelectrics 5, 39 (1973)
Table 1

Physical Properties of Piezofilms

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<tr>
<td>Pyroelectric Coefficient</td>
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<td>(1.75K/min)</td>
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FIGURE CAPTIONS

Fig. 1 - The pressure dependence of $d_p$ at different temperatures

Fig. 2 - The pressure dependence of $p_y$ at different temperatures

Fig. 3 - The temperature dependence of $d_p$ at different pressures

Fig. 4 - The temperature dependence of $p_y$ at different pressures

Fig. 5 - The pressure dependence of $T_g$ and $d_p$(minimum)

Fig. 6a - The pressure dependence of $d_p$ to $d_y$ (0-4 Kbar)

Fig. 6b - The pressure dependence of $d_p$ to $d_y$ (4-7 Kbar)
Figure 1

- $d_p \times 10^{12} \text{ (C/N)}$

- $48^\circ \text{C}$
- $24^\circ \text{C}$
- $0^\circ \text{C}$
- $-24^\circ \text{C}$
- $-48^\circ \text{C}$

Pressure (Kb)
Figure 2
Figure 3
Figure 4
TRANSITION TEMPERATURE (°C)

Figure 5
Figure 6a

$\frac{d_p}{P_y} \times 10^3 \text{(cm}^2\text{K/N)}$
Figure 6b