Resistivity and piezoelectric measurements on oriented and unoriented thick PVF_2 films

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INTRODUCTION

In order for polyvinylidene fluoride (PVF_2) to become strongly piezoelectrically active, it must be poled under a high electric field, 1 MV/cm of more if poled at room temperature. Since the permanent polarization of a PVF_2 specimen has been found to increase with the magnitude of the poling field, it is advantageous to use as high a poling field as possible as long as saturation has not been reached[1]. The limiting factor for using high fields is the breakdown strength of the material.

For the preparation of thick (250 μm or more) specimens of PVF_2, special requirements must be met because voltages up to 100 kV are used. Precautions are necessary in order to minimize corona, flashover conduction and breakdown. Corona and flashover problems are usually handled by carrying out poling in a dielectric oil. For thick samples prepared in this laboratory, breakdown became a potentially large problem when we observed that unoriented specimens had breakdown strengths of only 0.3 to 0.6 MV/cm. Initially, the low breakdown strength was attributed to an inherent property of thick sheets, i.e., breakdown strength was lower for a thick sheet than for a thin sheet because the probability of including a flaw or a source of breakdown increases with thickness. Further investigations, however, showed that there was a large difference between mechanically oriented and unoriented PVF_2 material. The oriented material is able to withstand poling fields of 1 MV/cm so that acceptable transducer activity can be achieved. Another advantage of orienting PVF_2 is that it is possible to achieve an enhanced piezoelectric activity if the mechanical draw ratio is larger than the 4:1 natural draw ratio[2].

In this report, we investigate the difference in electrical properties of oriented and unoriented PVF_2 by measuring resistivity and by poling both oriented and unoriented PVF_2 samples.

SAMPLE PREPARATION

The material for these specimens came from two sources: sheet material of two thickness, 0.154 cm and 0.051 cm, from Pennwalt Corp. and PVF_2 powder (Solef XP8N) from Soltex Chemical Co.* The powder was moulded into a disc shape by using a vacuum mould at 175°C. Oriented specimens were obtained by stretching on a tensile testing machine at temperatures between 60° and 80°C at a draw rate of 0.7 cm/min.

RESISTIVITY MEASUREMENTS AND RESULTS

In order to examine the difference between the electrical properties of oriented and unoriented PVF_2, we chose to measure resistivity. Each specimen was prepared by painting on it three silver paint electrodes, namely centred electrodes on each side and guard ring around one of the centred electrodes. The guard ring was used to shunt off surface currents. Measurement of the current through the sample was obtained by observing the voltage drop across a 10^6 ohm resistor in series with the specimen. The source voltage was either 100 V or 1000 V as was required for a sensitive response. The accuracy and precision of the resistivity measurement are estimated to be $\pm 10\%$.

The results of the resistivity measurements are shown in *Table 1*. Here, the value 2.2×10^{17} ohm-cm was the limit of sensitivity for the specimens 1PW-3 and 1PW-5. The data distinctly show the resistivity for unoriented PVF_2 are lower than those for the oriented material by at least an order of magnitude. It is apparent that the state of orientation is an important factor which affects the electrical properties of PVF_2.

PIEZOELECTRIC MEASUREMENTS AND RESULTS

The hydrostatic piezoelectric coefficient d_p and the pyroelectric coefficient Py were measured using a copper cell which has been described in the literature[3]. With this cell, the Py coefficient is measured by observing the current response accompanying a temperature change of approximately 2°C. The d_p coefficient is measured by observing the current generated in response to a pressure change. The accuracy of the d_p and Py measurements is estimated to be $\pm 10\%$; the precision for d_p and Py is $\pm 5\%$.

Piezoelectrically active samples were obtained by poling under oil at room temperature and at 80°C. Two oils have been used with satisfactory results. They are a

Table 1 Resistivity measurements

Sample	Condition	Resistivity
R-PW	Unoriented	1.99×10^{15} ohm-cm
PW (0.152)	Unoriented	1.78×10^{15} ohm-cm
S-1	Unoriented	2.35×10^{15} ohm-cm
1 PW-3	Oriented	$>2.2 \times 10^{17}$ ohm-cm
1 PW-5	Oriented	$>2.2 \times 10^{17}$ ohm-cm
3 PW-2	Oriented	5.5×10^{16} ohm-cm
6 PW-a	Oriented	5.4×10^{16} ohm-cm
6 PW-c	Oriented	4.2×10^{16} ohm-cm
S-2	Oriented	1.13×10^{17} ohm-cm

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* Identification of a commercial product is made only to facilitate experimental reproducibility and does not imply endorsement by NBS

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Table 2 Pyro- and piezoelectric coefficients of thick samples

Sample	Thicknesses (cm)	Poling conditions	$P_y \left(\frac{nC}{cm^2K}\right)$	$d_p \left(\frac{pC}{N}\right)$	$d_p/p_y \left(\frac{cm^2K}{N}\right)$
S-1	0.035	0.6 MV/cm, 80°C, 20 min	0.64	–	
1 PW-3	0.023	1 MV/cm, R.T., 1 h	1.31	6.8	5.19×10^{-3}
1 PW-4	0.028	1.5 MV/cm, R.T., 30 min	2.3	11.8	5.13×10^{-3}
1 PW-5	0.026	1 MV/cm, 85°C, 30 min	2.0	9.2	4.60×10^{-3}
3 PW-2	0.027	1 MV/cm, 85°C, 20 min	2.7	10.5	3.89×10^{-3}
6 PW-a	0.009	1 MV/cm, 85°C, 20 min	2.11	8.21	3.89×10^{-3}
6 PW-b	0.0095	1.5 MV/cm, 85°C, 20 min	1.85	8.1	4.38×10^{-3}
7 PW-a	0.073	0.5 MV/cm, 80°C, 30 min	0.5	3.15	6.30×10^{-3}
10 PW-a	0.060	1.4 MV/cm, R.T., 30 min	2.57	13.8	5.37×10^{-3}
11 PW-b	0.065	1.3 MV/cm, R.T., 12 min	2.0	10.5	5.15×10^{-3}

silicone oil and an alkyl benzene dielectric oil.

A field of 1.3 MV/cm across the 0.065 cm specimen was achieved by applying 85 kV. In order to minimize the problem of surface flashover, the poling oils are degassed and filtered into a closed poling vessel. It was found that the oils could be reused as long as they were pulled through a filter with a 20 μm pore size or less. Also helpful in preventing flashover is a large apron of sample extending beyond the electroded portion of the specimen. Because of dimensional and size constraints on the stretched specimens, a large apron was not always possible.

At first, evaporated Al electrodes were used but it was found that these peeled off when the specimen was immersed in oil at 80°C or they were burnt off during surface flashover. Subsequently, silver point electrodes were found to adhere well at 80°C and were able to withstand surface flashover without disintegrating.

Those samples which appear in *Table 1* but not in *Table 2* either broke down during poling or were not poled. All samples in *Table 2*, with the exception of sample S-1 are in the oriented condition.

DISCUSSION

The unoriented specimens, for which resistivity measurements were made, could not be poled at high fields because of their low breakdown strength. Only one sample, S-1, survived a moderate poling field of 0.6 MV/cm. The piezoelectric activity for this specimen is correspondingly low.

In *Table 2* we have listed the value of the ratio d_p/Py. These numbers vary from 3.89×10^{-3} to 6.30×10^{-3} cm^{2}K/N. Such a wide range of values for this ratio is in contradiction to the nearly constant value of 4.8×10^{-3} cm^{2}K/N which was observed by Kenney[1]. This difference is probably brought about by the fact that Kenney's specimens were morphologically uniform having been taken from the same sample lot, whereas the specimens used in this study were prepared from resin of two types and stretched at temperatures ranging from 60° to 80°C.

There is not enough information in the present study to propose a model describing the change in resistivity of PVF_2 upon stretching. For other halogen containing polymers, the conducting species has been identified as ionic carriers whose transport properties are affected by polymer morphology[4].

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