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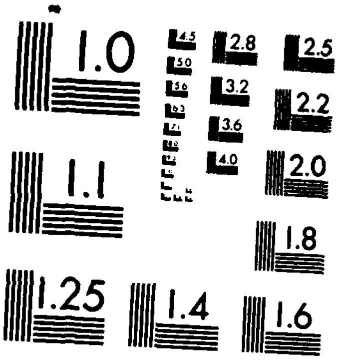

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Executive Summary

It has been established that space charge effects are important in determining the polarization distribution of ferroelectric polymers when these are poled under conditions of significant, though still extremely small, conductivity. Asymmetric distributions are observed and these are indicative not only of space charge present during poling but also of polarity-dependent barrier effects at the metallic electrode-polymer interfaces.

Among the polymers surveyed in this contract which gave simple asymmetric polarization profiles, PVF_2 and $P(VF_2\text{-}TFE)$ showed a tendency to pole most strongly in the regions near the poling anode indicating accumulation of negative charge during poling, while PVF and Nylon 11 tend to pole most strongly near the poling cathode, indicating accumulation of positive charge. The difference among samples in the sign of the charge accumulated during poling suggests that a basic relation exists between cha~~n~~rging behavior and bulk or surface polymer structure; however, additional work is required to establish the nature of such a relation.

Under conditions of negligible conductivity, the observation of nonuniform sample properties are suspected to be of morphological origin or due to pre-existing polarization of unknown origin. However, it appears that under these conditions, the polarization distributions are nominally symmetric.

The effects of work-function differences between metallic electrodes and polymer samples poled at room temperature were found to be unobservable as they were smaller than those of sample inhomogeneities.

Studies of electron-beam irradiated PVC have revealed interesting, new information-storage properties of this material. The information is observed as an inhomogeneous pyroelectric activity profile which is believed to be closely related to the electric field profile existing in the material during irradiation and producing a radiation-induced polarization. However, at doses sufficient to produce radiation damage, the pyroelectric profile can be affected by radiation-induced nonuniformities of the thermal expansivity profile.

Keywords: Piezoelectric Polymers, Pyroelectric Polymers.

FINAL REPORT

Statement of Problem Studied

The problem studied was the charging and polarizing of polymers subjected temporarily to high electric fields or irradiated by an energetic beam of electrons. The main goal of the work was to gain an understanding of space-charge phenomena (injection, transport and accumulation) in representative polymers, and of their effect on internal electric fields. Factors which were deemed potentially relevant included interfacial effects stemming from work function differences between polymer samples and metallic electrodes, bulk electronic structural properties and dynamic effects involving weak electric conductivity.

The chief tool used in the work was the thermal pulse polarization versus depth profiling method[1,2] which is well suited for samples of thickness in the range 10 to 150μm. This thickness range allows near breakdown poling fields to be produced in the samples with externally applied voltages between 1 and 20 kV which are easily managed.

The main polymers studied included ferroelectric polyvinylidene fluoride (PVF_2), polar polyvinyl chloride (PVC), Nylon 11, and nonpolar polymers such as polyethylene (PE) and fluoroethylene propylene (FEP).

Summary of Important Results

The evolution of the polarization distribution in PVF_2 as the poling field is progressively increased, decreased and reversed, was studied extensively. Previous work at NBS and elsewhere on PVF_2 samples poled at relatively high temperatures (*ca.* 100C) and on $P(VF_2\text{-}TFE)$ copolymer samples poled at room temperature or above show a tendency for polarization to be asymmetrically distributed and generally to occur with greatest strength in the regions adjacent to the electrode which was positive during poling (the poling anode). In particular, for weak poling fields, the polarization was found to vary from a maximum near the poling anode to zero near the poling cathode. The above-described results can be understood, perhaps naively, within a model involving the accumulation of negative charge carriers in the bulk during poling. Within this model, the electric field of the excess carriers adds to the applied field on the side of the poling anode and subtracts from the applied field on the side of the poling cathode. In this way, the resulting poling field acquires the asymmetric distortion from uniformity which results in the observed nonuniform polarization. The accumulation of a steady state negative charge distribution during poling requires the action of voltage and polarity-dependent barrier properties at the metal-polymer interfaces. These properties allow charge injection or ejection in a manner reminiscent of the Schottky effect. In addition, significant mobility of the injected charge is required. An alternative model involving displacement of preexisting positive and negative carriers within the bulk of an electrically neutral sample with no charge transport across the metal-polymer interfaces is not expected to produce zero field near either surface, by Gauss's law.

Our thermal pulse results[4] on samples poled at room temperature gave rather symmetric and poling voltage dependent polarization distributions with a broad maximum in the middle regions of the samples. At zero and low poling voltages, the results showed little polarization near the surfaces, as well as extraneous effects indicative of preexisting polarization in nominally unpoled samples. The evolution of the polarization distribution when the poling voltage was gradually increased to high values and subsequently was reversed showed clearly that the central parts of the sample switched more readily than the regions near the surfaces.

The most readily apparent and seemingly relevant difference found between samples showing symmetric and asymmetric polarization distributions is their electric resistivity at the poling temperatures. Samples which gave symmetric distributions had resistivities of order 10^{14} Ωcm while those which gave asymmetric distributions had resistivities of order 10^{11} Ωcm. To our knowledge, no experimental data are available on the dependence of charge injection properties on temperature in polymers. Materials with electronic band gap differences of order 1eV are not expected to give strongly temperature dependent barrier properties between room temperature and 100C. However, polymers could have a near-continuum of electronic defect states or impurity states within their gaps, and these states could bring about temperature dependence of the injection properties.

An attempt was made to detect barrier properties by varying the electrode metal and thus the electronic work function difference between metal and polymer. Reports in the literature[5,6] had led us to believe that work function effects should be readily apparent. It was found[7] that this was not the case for PVF_2 samples poled at room temperature. Although samples with a variety of electrode metals showed different skewed distributions of polarization, a survey of a large number of polarization distributions showed a tendency for the distributions to be classifiable into two categories (skewed towards one side or the other) independently of electrode materials. This observation opened the possibility that the skewness was associated with nonuniformities of the sample properties.

This possibility was tested by doing experiments using duplicate samples for each electrode combination to allow keeping track of the front-back orientation of each sample. Denoting the orientation of a sample arbitrarily by the outward normal to the surface which was convex before the sample was taken from a roll, it was confirmed that the skewness of the distribution depended on the direction (parallel or antiparallel) of the applied field relative to the outward normal and did not depend in a consistent manner with the electrode combination.

The obvious experiment of repeating all the measurements with different electrodes using elevated poling temperatures was not done. However, based on the measurements to date, it appears that work function effects and conductivity effects do not affect significantly the poling electric field distribution in PVF_2 samples poled at room temperature.

Measurements of polarization distributions in the other materials cited indicated that materials differ in the sign of the charge which they accumulate under a strong applied field. As already stated, PVF_2 and $P(VF_2\text{-}TFE)$ tend to accumulate negative charge. The same was found to be true for FEP. On the other hand, Nylon 11, like PVF which we previously studied[8], tends to accumulate positive charge. PE is rather special and requires detailed study as the sign of the charge it tends to accumulate under a high field appears to depend on temperature.[9] This observation is significant for power cable applications. A more-indepth study of PE by the thermal pulse method is currently under way under separate funding from the Electric Power Research Institute.

Polarization distribution measurements in electron-beam charged PVC gave signals consistent with the presence of weak and nonuniformly distributed polarization.[10] Polarization in general gives a nonzero asymptotic response which is the normal pyroelectric response. (Ordinarily, real charge is expected to give zero asymptotic response). Analysis of the thermal pulse signals yields a polarization profile varying from a positive maximum on the irradiated surface to a negative maximum on the opposite surface. The electron energy used was 100KeV and sample thickness was 125µm. It is believed that the electrons penetrated substantially across most, if not all, the thickness.

The thermal pulse signals were found to be unstable for several days after irradiation. However, after this initial discharge period, the thermal pulse signals stabilized and remained stable indefinitely afterwards based on observations for at least one year after irradiation. A simple explanation for the results is that the electron-beam deposited charge inside a sample produces a high and nonuniformly distributed electric field which induces nonuniform polarization across the sample. The shape of the measured polarization distribution is consistent with expectations for the shape of the electric field during irradiation. The polarization was relatively weak because the irradiation was done on samples at room-temperature which is well below the glass transition temperature of 60°C.

Since PVC is not expected to pole significantly below Tg when a field is produced by an applied voltage, it is likely that the observed polarization is a real radiation-induced effect. The radiation-induced polarization is stable as long as the sample is kept well below Tg. As for the charge deposited by irradiation, it disappears after a few days.

Other explanations for the thermal pulse results on electron irradiated PVC were also considered. For example, an implanted charge distribution, if combined with radiation-induced nonuniform thermal expansivity could give a pyroelectric-like (nonzero) asymptotic response.

It is theorized that at low radiation doses (low radiation damage regime), the polarization mechanism in electron irradiated PVC will be similar to that which occurs under an applied voltage. In that regime, the measured polarization after irradiation should represent a record of the electric field during irradiation. Since PVC is a linear dielectric (not a ferroelectric), the polarization at any depth should be proportional to the peak radiation-induced field at that depth. On the other hand, at high radiation doses (radiation-damage regime), thermal properties and other properties will be affected locally in proportion to local dose, in which case permanently implanted charge can contribute to the response.

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"Poling behavior of polyvinylidene fluoride at room temperature" by F. I. Mopsik and A. S. DeReggi, Appl. Phys. Letters 44, 65 (1984).

"Preexisting polarization and influence of electrode materials on PVF_2 electrodes as determined by thermal pulse and pyroelectric methods" by S. B. Lang, A. S. DeReggi, F. I. Mopsik and M. G. Broadhurst, J. Appl. Phys. 54 5598 (1983).

"Transduction phenomena in ferroelectric polymers and their role in biomedical applications" by A. S. DeReggi, Ferroelectric 60, 83 (1984).

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