

THERMAL DEPOLARIZATION OF PVDF: ANOMALY AT 180°C

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Abstract

PVDF samples with high β -content (80%), prepolarized at room temperature, are heated to higher temperatures. The polarization is measured first under open circuit conditions at the high temperature and then after cooling down again to room temperature. For elevated temperatures up to 175°C the polarization is reduced to 2% of the original value, yet recovers roughly to 8% of the original value after cooling down again to room temperature. In contrast to this when heating up the films to 180°C a significantly different behavior is observed: In cooling down to room temperature again the polarization returns from about 1% at 180°C to about 40% of the original prepolarized value.

Introduction

Compared to other polymers PVDF shows high piezo- and pyroelectricity [1,2] which is caused by the formation of a remanent polarization in the crystallites of the polar β phase by applying electric fields exceeding 50 MV/m. This is theoretically described by the rotation of the polymer chains in steps of 60° caused by the pseudo hexagonal structure of the β crystallites [3,4,5]. The times which are necessary for dipole orientation in an external electric field calculated by the 60° model [6] agree well with the measured times [7]. Yet so far no prediction about the stability of the remanent polarization after switching off the electric field has been made. Instead it has been assumed that the polarization remains constant after removing the external electric field as consequence of the anisotropy of the crystal field and of the cooperative interaction of the dipoles [5,8]. More recent measurements indicated that the alignment of the dipoles in field direction and the stability of the remanent polarization have different time constants in pure PVDF [9] and in the P(VDF/TrFE) copolymer [10]. This implies that the 60° model has to be supplemented by mechanisms which describe the stability of the remanent polarization. Measurements with blocking electrodes showed that the polarization is only stabilized if charges are injected and trapped at the surface of the crystallites [12]. From this it has been conjectured

that the stability of polarization in PVDF at room temperature is caused by the coulomb interaction of the dipoles with these trapped charges. In order to investigate the binding energies of the charges we measured the temperature dependent decay of the remanent polarization. This thermal depolarization is studied by measuring the polarization at the elevated temperature and also after cooling down again to room temperature.

Experimental

Our samples were biaxial stretched, 38 μm thick PVDF films with high β content (80%). The samples were poled at room temperature at $E = 200 \text{ MV/m}$ for 5s. After poling they were kept under short circuit conditions for several minutes. The remanent polarization at room temperature was measured with the PPS method [12,13]. Then the temperature was increased and the polarization was measured again at high temperature. The PPS apparatus was placed into an oven. Immediately after measuring the remanent polarization at high temperature the door of the oven was opened and the sample was cooled down to room temperature. At room temperature the remanent polarization was measured for the third time, without removing the sample from the PPS apparatus. The surfaces of the sample were under DC high ohmic open circuit conditions during the measurements described above.

The pressure caused by the piston which presses the polymer film against the piezo crystal of the PPS apparatus prevents the samples from shrinking. Shrinking was expected because the polar β phase which results from stretching is changed to the non polar α phase if the films are annealed to high temperature [14]. Thus the thickness of the samples remains almost constant even until 180°C if they remain in the PPS apparatus during heating.

Measurements

Figure 1 shows the results for a series of 16 samples heated to different temperatures up to 180°C. The triangular points show the polarization of each sample after prepolarization. Selected were samples with a polarization of $(5.4 \pm 0.1) \mu\text{C}/\text{cm}^2$ to eliminate sample fluctuations. The circles show the measured polarization at high temperatures and the stars the polarization of the same sample after cooling down to room temperature. At each temperature a new sample was used. The "Remanent polarization" in figure 1 corresponds to the maximum value of the polarization within the film thickness. With increased heating temperature the polarization decreases slowly from $5.4 \mu\text{C}/\text{cm}^2$

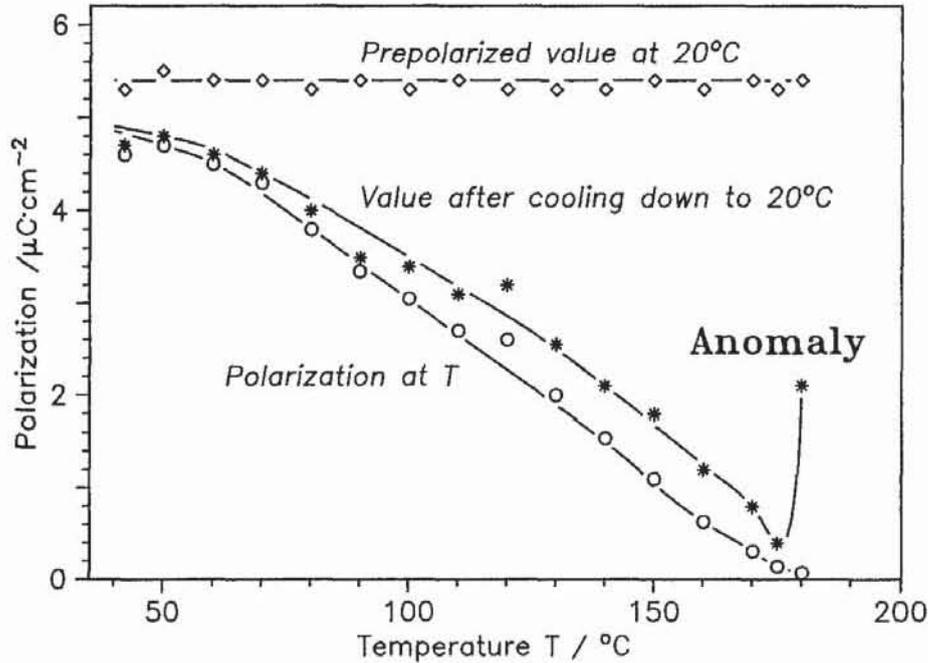


Figure 1: Thermal depolarization of PVDF. Represented is the remanent polarization of each sample after poling at room temperature \diamond , the polarization at high temperature \circ and after cooling down to room temperature $*$.

at 20°C to $4.3\mu\text{C}/\text{cm}^2$ at 70°C. The difference in polarization at high temperature and after cooling down to 20°C is small compared to the polarization reduction above 70°C. Between 120°C and 170°C the absolute difference of these two values remains almost constant whereas the high temperature polarization tends to zero at 180°C. The ratio of the polarization after cooling down to room temperature compared to the polarization at high temperatures increases from 1.05 at 80°C to 1.23 at 120°C and finally to 2.85 at 175°C.

When the temperature is increased to 180°C a significant change of the behavior is observed when the sample is cooled down to room temperature. The measured polarization at 180°C amounts to $0.07\mu\text{C}/\text{cm}^2$ at. This is about 1% of the prepolarized value. Yet if the sample is cooled down to room temperature again the polarization unexpectedly increases to $2.1\mu\text{C}/\text{cm}^2$ which is about 40% of the prepolarized value. In contrast to this by cooling down from 175°C to room temperatures the polarization recovers from $0.14\mu\text{C}/\text{cm}^2$ to only $0.4\mu\text{C}/\text{cm}^2$.

The anomalous increase of the polarization by cooling down from 180°C means that polarization which has almost disappeared before arises again. The ratio of the polarization after cooling down from 180°C to 20°C is 30! This is significantly larger than the ratio of 2.85 by cooling down from 175°C.

The anomaly described above was observed for several samples. The measurements described were made with PVDF films supplied in 1988 by Solvay + Cie. Newer films with higher crystallinity supplied in 1990 by the same source show this behavior, too. By cooling these new films the polarization rises from $0.24\mu\text{C}/\text{cm}^2$ at 180°C to $4.1\mu\text{C}/\text{cm}^2$ at 20° and from $0.5\mu\text{C}/\text{cm}^2$ at 175°C to $1.9\mu\text{C}/\text{cm}^2$ at 20°C. Figure 2+3 show the temperature dependent increase of the polarization of these newer films by cooling down from 180°C (figure 2) and from 175°C (figure 3). In figure 2 a strong increase of the polarization between 170°C and 150°C from $0.34\mu\text{C}/\text{cm}^2$ to $2.1\mu\text{C}/\text{cm}^2$ is seen. By further

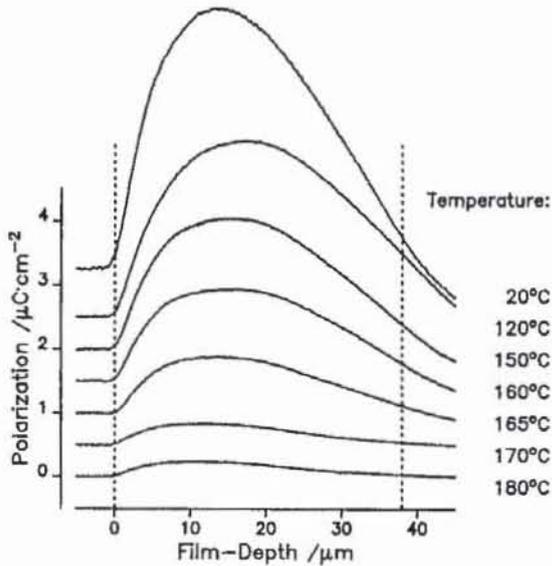


Figure 2: PPS measurement of the polarization distribution by cooling a prepolarized PVDF sample down to room temperature after heating up to 180°C

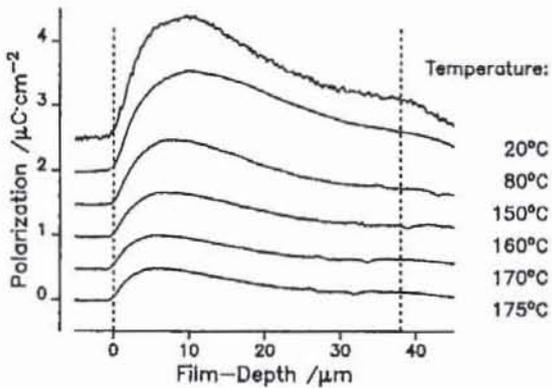


Figure 3: PPS measurement of the polarization distribution by cooling a prepolarized PVDF sample down to room temperature after heating up to 175°C

cooling to room temperature the polarization grows slower until $4.1\mu\text{C}/\text{cm}^2$ at 20°C . In contrast to this by cooling down from 175°C the strong increase between 170°C and 150°C is not observed (figure 3). In this case a continuous recovery of the polarization from $0.5\mu\text{C}/\text{cm}^2$ at 175°C to $1.9\mu\text{C}/\text{cm}^2$ at 20°C is observed.

Unpoled films show no polarization after heating and cooling. But if a voltage is applied to unpoled films at 175°C and the films then heated up to 180°C an electric breakdown occurs between 179°C and 180°C , even if the voltage is smaller than 10V. Simultaneously the film thickness decreases at this temperatures. At temperatures between 175°C and 179°C 300V could be applied to the films without electric breakdown. If a voltage is applied to unpoled samples during cooling down from 179°C to room temperature a remanent polarization arises again. But this polarization is distinct smaller than the polarization after cooling down prepolarized samples from 180°C to room temperature. For example at 300V applied during cooling $0.8\mu\text{C}/\text{cm}^2$ at the older films and $2.0\mu\text{C}/\text{cm}^2$ at the newer films was measured at room temperature. To form the same polarization under an external electric field as in the experiments described above field strengths of more than 10MV/m are necessary. If the same depolarization experiments are made under short circuit conditions, i.e. the sample surfaces are connected with an ohmic resistance of $3.3\text{k}\Omega$, no principle change is observed during heating and cooling down from 180°C to room temperature. At the new film material the polarization recovers from $0.34\mu\text{C}/\text{cm}^2$ at 180°C to $4.0\mu\text{C}/\text{cm}^2$ at 20°C . These experiments indicate that no macroscopic field is necessary for the recovery of the polarization during cooling.

Conclusion

If prepolarized PVDF films are heated up in the temperature range from 40°C to 180°C the remanent polarization decreases by thermal depolarization. If the films are cooled down to room temperatures again before the heating temperature reaches 180°C the difference of the remanent polarization at high temperature and at room temperature can be due to the higher thermal agitation of the crystallite dipoles. If the heating temperature is increased to 180°C an anomalous increase of the polarization is observed after cooling which cannot be explained by this thermal agitation. The also observed change in film thickness and the electric breakdown of non polarized films under low voltage indicate that the melting point of the crystallites in the films is

reached at about 180°C. But at this temperature the polarization in prepolarized films does not disappear completely. This indicates that the crystallites do not melt completely at 180°C in prepolarized films. Therefore in cooling crystallisation nuclei are present with preference direction in which the crystallite dipoles are oriented when the films recrystallize. The recrystallization occurs apparently between 170°C and 150°C, leading to the strong increase of the remanent polarization as observed in this temperature region. Since in thermal depolarization the polarization is continuously reduced in a broad temperature region this can be attributed to a wide distribution of the binding energies of the trapped charges. This is conceivable as the traps are located at the boundaries of the crystallites and the amorphous phase. In these systems a broad energy-distribution is expected.

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