

DYNAMICS OF POLING PVDF BETWEEN 25°C AND 120°C

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Abstract

PVDF films with high β -content are poled in an electric field of 60 MV/m at temperatures between 25°C and 120°C. At 25°C the alignment of dipoles takes place in a central poling zone during some hours of poling. When the temperature is increased to 120°C the poling time necessary to align the dipoles in this narrow zone is reduced to some seconds. In addition to this at temperatures higher than 90°C and increased poling times the central poling zone first increases but later decreases in its dielectric displacement. Simultaneously in a 10 μ m regime adjoining the positive electrode a secondary displacement zone starts to grow. The strong reduction of this peak under short circuit condition indicates hetero-charge accumulation in front of the anode.

Introduction

The strong pyro- and piezoelectricity of PVDF compared to other polymers give rise for many applications for example as infrared and ultrasonic detectors [1]. Both effects are caused by the formation of a remanent polarization after poling in electric fields greater than 50 MV/m. In contrast to crystalline ferroelectric materials PVDF films are not always homogeneous poled, but in dependence on poling field strength and α and β form crystallites thin, only some μ m thick polarization zones are formed [2,3,4]. For α PVDF a thin polarization zone at the anode is observed, while for β PVDF a central polarization zone is formed by poling at $E = 60$ MV/m [5]. With the PPS technique the dynamics of the formation of these thin polarization zones are well investigated [5,6,7]. It has been shown that injection, migration and trapping of charges determine the position and thickness of these polarization zones. But till now these investigations were limited at room temperature. By poling at higher temperatures it is expected that the formation of the polarization is faster compared to room temperature because of easier chain rotation and higher mobility of the charge carriers [8]. To investigate the

polarization dynamics at temperatures between 25°C and 120°C is the object of this work. In addition to this its of interest, whether the polarization profile changes because of the higher charge carrier mobility. This could happen because the injected charges determine the position of the polarization zone as well as the stability of the remanent polarization is caused by trapped charges at the surfaces of the crystallites [10]. On the other hand from the temperature dependent change of the polarization profile we want to determine the binding energy of these trapped charges and their nature.

Experimental

The spatial distribution of charges and polarization in PVDF between 25°C and 120°C was measured with the PPS technique [7,9]. Therefore the PPS apparatus was put into an oven which was kept at constant temperature during measuring. A HV pulse with rise time less than 1ns applied to a quartz disk produces a pressure step which is coupled into the PVDF film and propagates with sound velocity. Charges and polarization are displaced and deformed by the propagating pressure step. The corresponding displacement current in an outside circuit is measured with a broad band amplifier and displayed on a real time TEK 7104 oscilloscope. The oscilloscope screen is recorded on a video tape and the PPS signal is later digitized. With this method very slow changes in the PPS signal for some hours as well as fast changes shorter than 100ms can be observed. A thin, 25µm thick, Al-evaporated and high isolating PET film was inserted between the PVDF sample and the measuring electrode. With its help HV can be applied to the sample during the PPS analysis. The thin PET film doesn't change the shape of the signal because it acts as a wide band coupling capacitor. A conducting rubber electrode on the films serves for better electric coupling to the measurement circuit.

Measurements

a.) Poling at 25°C

Figure 1 shows the formation of a 15µm thick polarization zone by poling a 38µm thick, Al-evaporated film with about 80% β crystallites at $E = 60$ MV/m. Shown is the dielectric displacement under external field at different poling times and the remanent polarization after 900s under short circuit conditions. Is after applying the electric field charges are on both electrodes. After 100s homo-charges are injected in a 5-10 µm thick zone near the anode.

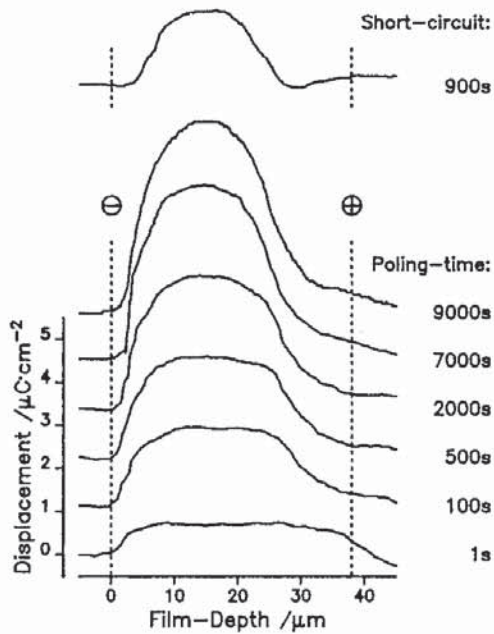


Figure 1:
Polarization dynamics by poling a 38 μm thick PVDF film at 25°C, $E = 60\text{MV/m}$, and after 2500s under short circuit conditions.

Therefore the displacement is increased in the rest of the film. Polarization rises at longer poling times until 9000s in a zone between 5 μm and 20 μm film depth. By shortening the sample free charges has vanished after the dielectric relaxations time of about 100s. After 900s under short circuit half of the value of the displacement under field remains as remanent polarization [11].

b.) Poling at 118°C

If the temperature is increased to more than 100°C the formation of the about 15 μm thick polarization zone occurs within few seconds of poling. Figure 2 shows the time dependent development of the dielectric displacement by poling the same 38 μm thick β PVDF film material at 60 MV/m at 118°C. Figure 2 shows that in contrast to the former measurement positive charges are injected in a 15 μm thick zone in front of the anode and negative charges are injected into a 5 μm thick zone in front of the cathode after some seconds of poling.

As expected the time development of the polarization occurs faster when the temperature is increased from 25°C to 118°C. The situation after 1s of poling at 118°C correspond to the situation after 9000s of poling at 25°C. This corresponds to a reduction of the time constants for polarization and charge transport by four orders of magnitude. The lower experimental limit of the time constant measurement is 1s, the rise time of the HV power supply.

After 10s poling time the displacement increased between 5 μm and 20 μm film

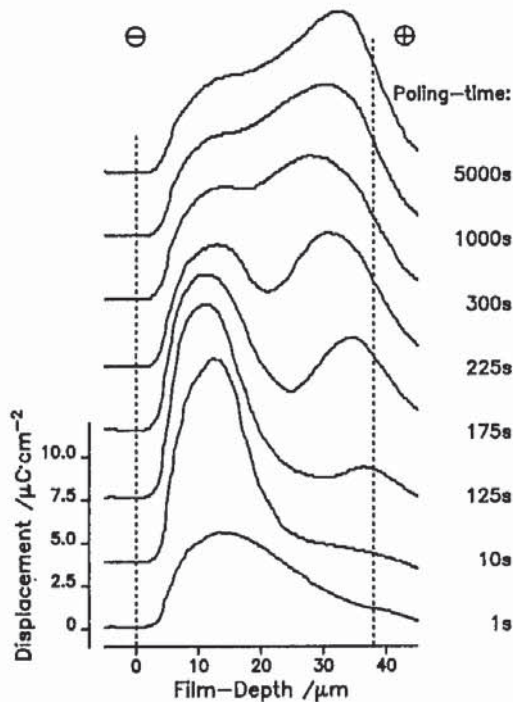


Figure 2:

Polarization dynamics by poling a 38 μm thick PVDF film at 118 $^{\circ}\text{C}$, $E = 60\text{MV/m}$

depth to about 12 $\mu\text{C}/\text{cm}^2$, a value which has never been reached at room temperature at this field strength not even after one day of poling [12]. In contrast to this the polarization profile doesn't change until 100s poling time. At 125s poling time the profile alters. In front of the anode in a second 15 μm thick zone the dielectric displacement begins to grow. Between 125s and 300s this second zone grows fast, in the following time until 5000s slower. But in contrast to the growing of the first zone this process is very slow. Simultaneously to the growing of the second zone the dielectric displacement in the first zone decreases from 12 $\mu\text{C}/\text{cm}^2$ at 100s to 6.2 $\mu\text{C}/\text{cm}^2$ at 300s and at last to 5 $\mu\text{C}/\text{cm}^2$ at 5000s poling time. During this time the second zone increases to 9.1 $\mu\text{C}/\text{cm}^2$. Very interesting is the formation of a "Double-Hump-Structure" between 125s and 300s.

Figure 3 indicates that there are also differences by shortening the sample at 118 $^{\circ}\text{C}$ compared to 25 $^{\circ}\text{C}$. The first polarization zone between 5 μm and 20 μm decreases from 5 $\mu\text{C}/\text{cm}^2$ at 1s to 4 $\mu\text{C}/\text{cm}^2$ at 1000s short circuit. In contrast to 25 $^{\circ}\text{C}$ the first polarization zone remains nearly unchanged. On the other hand the second polarization zone in front of the anode decreases faster during the first hundred seconds short circuit to 4.3 $\mu\text{C}/\text{cm}^2$ and slower until 1000s to 3.3 $\mu\text{C}/\text{cm}^2$. In the second zone remains less polarization remanent compared to

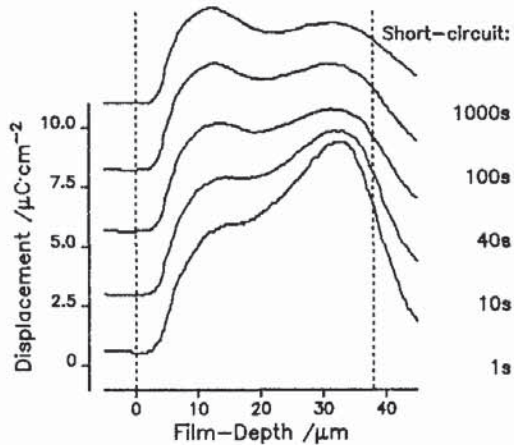


Figure 3:
The same sample as in figure 2
under short circuit condition.

the first zone. The "Double-Hump-Structure" is again recognizable.

Conclusion

By poling β PVDF at 60 MV/cm homo-charges are injected into the film from both electrodes. These charges enhance the local electric field in the film and the crystallite dipoles are aligned in this field. Simultaneously a part of these charges are trapped at the crystallite surfaces. If the temperature raises from 25°C to 120°C this process is speeded up by a factor 10000. Dipole alignment and charge trapping hinder the movement of the free charges to the other electrode. Therefore no migration of the free charges through the polarization zone was observed at room temperature. On the other hand at 120°C negative space charges enter the polarization zone during some minutes of poling. This causes a decreasing of the dielectric displacement in this zone. If the negative charges have passed this zone they move very fast to the other electrode and are accumulated in a 10 μ m thick zone in front of the anode. If the sample is shorted these accumulated charges recombines with their compensation charges during some minutes. The PPS signal decreases. In the field of these accumulated charges dipoles are oriented, too. In the first polarization zone the PPS signal under field after 5000s poling time nearly originates from the alignment of the crystallite dipoles. Therefore the signal decreases only a little bit under short circuit in the first polarization zone. The binding energy of the trapped charges so far has not been investigated.

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