Non-uniform polarization profiles in P(VDF-TrFE) copolymer films after cyclical poling

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Abstract— Poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) copolymers, probably the most often used electro-active polymers, are rendered ferro-, pyro-, and piezo-electric via poling under high electric fields. Uniform polarization profiles across the sample thickness are advantageous or even necessary for most device applications. Here, we attempted to obtain spatially uniform polarization profiles in commercial P(VDF-TrFE) copolymer films with 50/50, 72/28 and 75/25 mol% of VDF/TrFE by means of cyclical hysteresis poling. The polarization profiles were mapped with Piezoelectrically generated Pressure Steps (PPSs), and the resulting depth profiles were correlated with the corresponding hysteresis curves. In addition, Fourier-Transform Infrared (FTIR) spectroscopy was used to identify the β -phase fractions in the P(VDF-TrFE) compositions. 75/25 mol% copolymer samples show the most uniform polarization profiles and the highest remanent polarization of 70 mC/m² (as seen from the hysteresis curves) – corresponding to the highest β -phase fraction in comparison (as observed in FTIR measurements).

Keywords— P(VDF-TrFE) copolymer; ferroelectric polymer; cyclical hysteresis poling (a.k.a. “Bauer poling”); Piezoelectrically generated Pressure Steps (PPSs); spatial polarization profiles

I. INTRODUCTION

Since the discovery of piezoelectricity in Polyvinylidene fluoride (PVDF) in 1969 [1], there has been extensive research with the aim of improving its piezo-, pyro- and ferroelectric properties. PVDF is utilized in many applications ranging from transducers to memory devices [2]. It is a semicrystalline polymer and exists in at least 5 different crystalline phases, namely the α -, β -, γ -, δ - and ϵ -phase [3,4]. Out of the 5 phases, the inherently polar β -phase PVDF has the highest (monomer) molecular dipole moment of 2.1 D. In the β phase, the polymer chains are arranged in a planar zig-zag (all-trans) conformation with all its molecular dipoles in the crystal lattice aligned in the same direction, leading to a rather high net electric polarization [5,6]. The non-polar α -phase is, however, the thermodynamically most stable crystalline modification when prepared by means of normal solution casting at room temperature. It was discovered that copolymerization of vinylidene fluoride (VDF) with trifluoroethylene (TrFE) monomers with a VDF molar content between 50 and 80 mol% leads to a copolymer of P(VDF-TrFE) that always crystallizes in the β conformation [5,7] which is desired in many practical applications owing to its easy preparation and its high piezo- and pyroelectricity. P(VDF-TrFE) copolymer has also been employed in several device applications, especially as transducers, energy-storage

capacitors [3,4] and organic field-effect transistors (OFET) for memory applications [8].

P(VDF-TrFE) film still needs to be poled under high electric fields to render it electroactive (*i.e.* piezo-, pyro-, and ferroelectric). The most common method to pole ferroelectric polymer electrets is corona poling. However, it is only suitable for applications which do not require high-precision poling [9], as corona poling does not always lead to uniform distribution of the electrical polarization throughout the poled polymer films [10,11]. Non-homogeneously poled PVDF and P(VDF-TrFE) films exhibit ill-defined transducer properties in particular with respect to their frequency behaviour – as highlighted in PVDF hydrophone [12] and second-harmonic generation applications [13]. One approach for homogeneous poling of ferroelectric polymer films is the so-called “Bauer cyclical poling method” [9,14,15]. It was done by forcing the film polarization through several hysteresis cycles, until a reproducible polarization hysteresis is achieved and extra space charge in the poled samples has been “drained off” [9,13,14]. The homogeneous distribution of polarization throughout the bulk of the poled film was proven with the pressure-wave propagation method (PWP) [14,16]. In the present paper, a similar procedure to Bauer cyclic hysteresis poling was used on commercial P(VDF-TrFE) films with different compositions.

The resulting polarization profiles were probed by means of Piezoelectrically generated Pressure Steps (PPSs) [17] to ascertain the effectivity of hysteresis poling. Hysteresis loops and polarization depth profiles of successfully poled P(VDF-TrFE) copolymer samples will be presented and discussed.

II. SAMPLES AND MEASUREMENT METHODS

A. Poly(vinylidene-trifluoroethylene) copolymer samples

Commercial P(VDF-TrFE) copolymer films with molecular compositions of 50/50, 72/28 and 75/25 mol% VDF/TrFE were provided by Piezotech SA in the form of thin films with a thickness of 30, 27 and 48 μ m, respectively. All films were metalized on both sides with circular aluminum electrodes (diameter ca. 12-15 mm, thicknesses 50-60 nm) for the polarization-hysteresis (Sawyer-Tower circuit), polarization-distribution and piezoelectric-coefficient measurements.

B. Polarization hysteresis with a Sawyer-Tower circuit

For poling of the P(VDF-TrFE) films with the Bauer cyclical poling method [9,14,15], polarization-hysteresis (*P-versus-E*

curves) monitoring in a Sawyer-Tower circuit was used [18]. A sequence of unipolar sinusoidal voltage curves (positive and negative direction) at a frequency of 1 Hz with maximum electric fields of 80 MV/m and 100 MV/m was used for hysteresis poling (cyclical poling process) [19]. The sample was subjected to the first 50 cycles at 80 MV/m, followed by another 50 cycles at 100 MV/m in order to achieve polarization saturation at the respective electric fields.

C. Spatial polarization-distribution measurements

Piezoelectrically-generated Pressure Steps (PPSs) [16,17, 20-22] were used to probe the spatial distribution of the electric polarization inside the sample film. Fig. 1 shows the working principle of the PPSs method. In this work, the PPSs signals are not calibrated (arbitrary units for the ordinate) so that only information about the polarization distribution along the thickness direction of polymer films is obtained. Comparison of the PPS signals from different samples with different thicknesses is thus not possible, since different sample thicknesses would require appropriate scaling of the overall PPS signal amplitudes. Each P(VDF-TrFE) copolymer film was equipped with aluminum electrodes (diameter ca. 12-15 mm) on both sides, which significantly increases the RC-time constant of the PPS signal [20]. In order to reduce the RC-time constant and to increase the signal bandwidth, an additional (non-electroded) poly(ethylene terephthalate) (PET) film with a thickness of ca. 12 μm was inserted between sample and rubber electrode in the PPS measurement [20]. The observed PPSs signal is a direct image of the polarization distribution in the thickness direction of the film under measurement [17]. For P(VDF-TrFE) copolymer films, a longitudinal sound velocity of 2.4 km/s was assumed [23].

D. Dynamical piezoelectric coefficient (d_{33}) measurements

After cyclical poling (Section B), the copolymer films were subjected to dynamic piezoelectric coefficient (d_{33}) measurements [24]. A static force of ca. 4-10 N was applied in order to ensure stable mechanical contact with the metal-plate electrodes of the dynamical piezoelectricity measuring setup. A measuring frequency of 2 Hz was used, and the average value of 6 consecutive measurements was recorded as the d_{33} coefficient of the respective sample.

E. Fourier-Transformed Infrared (FTIR) Spectroscopy and crystalline phases in the P(VDF-TrFE) copolymers

A Bruker Alpha-P® FTIR spectrometer operated in the ATR (Attenuated Total Reflection) mode at room temperature was used to investigate the chain conformations and the crystalline phases present in the P(VDF-TrFE) copolymer films with different molar compositions not only qualitatively, but also quantitatively.

III. RESULTS AND DISCUSSION

The FTIR spectra of the unpoled P(VDF-TrFE) copolymer samples with the three different compositions are shown in Fig. 2. The characteristic peaks corresponding to the different

Fig. 1. Measuring principle of the PPSs method (adapted from [20])

crystalline conformations of the copolymer chains are found in the 1500-400 cm^{-1} wavelength section of the FTIR spectra. According to the relevant literature [25-27], the wavenumbers of 1284, 879 and 842 cm^{-1} have been assigned to the polymer chains that are predominantly in the β phase. We can clearly see from the figure that the copolymer shows a strong absorption at these bands – indicating a dominant β phase in all three copolymers, as expected. Subsequently, the wavenumbers at 803, 763 and 613 cm^{-1} [3,28] usually associated with the crystalline fraction in the α phase do not manifest in the form of clear peaks in the spectra. The presence of a certain amount of γ phase is, however, observed via the peak at 505 cm^{-1} [29].

The fraction of the β phase in the individual copolymers with different compositions can be quantified by means of the procedure suggested by Gregorio and Cestari [30]. The values that were observed in our comparative study are found in Table I below. From the table, we can see that the copolymer with 25 mol% TrFE has the highest β -phase content of 87%, while the smallest β -phase fraction is seen in the copolymer with 50 mol% TrFE content. The higher fraction of β phase suggests that the 75/25 mol% should also possess superior electrical properties than the other compositions.

Figs. 3(a), 4(a) and 5(a) depict the polarization hysteresis of the P(VDF-TrFE) copolymer samples with 50/50, 72/28 and 75/25 mol% composition of VDF/TrFE, respectively, after 50 cycles of poling at 100 MV/m. It can be seen that all three compositions show a clear polarization hysteresis, although with different temporal behaviour. Out of the three compositions, the P(VDF-TrFE) copolymer with 75/25 mol% exhibits the highest remnant polarization (P_r) value of ca. 70 mC/m^2 at the end of the cyclical poling procedure – as shown in Table I, which corresponds to the fact that this composition shows the highest fraction of β phase and which also leads to a higher d_{33} coefficient (Table I). The P_r values obtained for the 50/50 and 75/25 mol% compositions are comparable to the

Fig. 2. FTIR absorption spectra of P(VDF-TrFE) copolymer films with different molar compositions.

values found in the literature [7,31] for similar compositions.

During cyclical poling at 80 MV/m, the hysteresis curves still continued to grow for all the three compositions at the end of 50 cycles. On increasing the field to 100 MV/m, the hysteresis curves for the 50/50 and 75/25 mol% samples saturated after poling for 10 cycles (Figs. 3 and 5), while the hysteresis curve still continued to grow for the 72/28 mol% composition up to the 50th cycle (Fig. 4). Following this, the 72/28 mol% sample was poled for additional 50 cycles at 100 MV/m, which again led to further growing hysteresis loops. The P_r values increased from 34 mC/m² at the end of 50 cycles to 44 mC/m² at the end of 100 cycles at 100 MV/m.

Furthermore, looking at the ferroelectric properties of the P(VDF-TrFE) films with 72/28 mol% as listed in Table I, and comparing it with the other two compositions, we observe that its properties are between those of the 50/50 and the 75/25 mol% compositions. It has been shown before that the ferroelectric properties increase with the increase in the TrFE ratio when the molar composition of TrFE is between 50 and 80 mol% [2]. All these findings seem to suggest that the ferroelectric polarization in the 72/28 mol% sample has not yet saturated and that a significantly higher number of cycles might be needed for this particular composition in order for the ferroelectric polarization to saturate and for the sample to arrive at similar d_{33} and P_r values as that of 75/25 mol%. However, one has to take into account also the fatigue behavior in the hysteresis curves when samples are poled for a higher number of cycles in the range of 100-1000 cycles [6,32,33].

Figs. 3(b), 4(b) and 5(b) show the spatial polarization profiles measured with the PPSs method for the 50/50, 72/28 and 75/25 mol% compositions, respectively, at the end of poling the samples at 100 MV/m for 50 cycles. From the figures, we observe that all three compositions show fairly non-uniform polarization distributions throughout their sample thickness. Especially for the 50/50 and 75/25 mol% compositions, even though the P_r saturates at the end of cyclical poling at 100 MV/m, the samples still show an inhomogeneous polarization profile. Again, out of the three compositions, the P(VDF-TrFE) samples with 75/25 mol% composition show a better spatial polarization distribution. Thus, we observe that the TrFE content not only influences the ferroelectric properties, but also the uniformity of the polarization across the sample thickness.

TABLE I. TABLE OF SAMPLE THICKNESSES, β PHASE CONTENTS (BEFORE POLING), REMANENT POLARIZATION (P_r) VALUES AND CALCULATED PIEZOELECTRIC (d_{33}) COEFFICIENTS AT THE END OF THE CYCLICAL POLING FOR THE DIFFERENT COMPOSITIONS OF THE P(VDF-TrFE) COPOLYMER

P(VDF-TrFE)	50/50 mol %	72/28 mol %	75/25 mol %
Sample thickness (μm)	30	27	48
β phase content (%) (from FTIR)	81	85	87
Remanent polarization (P_r) (mC/m ²)	35	34	70
Piezoelectric d_{33} coefficient (pC/N)	- 20	-10	- 27

Fig. 3. (a) Polarization- vs.-electric-field hysteresis curves for P(VDF-TrFE) copolymer samples with 50/50 mol% composition (tenth and fiftieth poling cycles) and (b) typical spatial polarization profile with the pressure step entering the sample at the electrode that was biased during poling.

Fig. 4. (a) Polarization- vs.-electric-field hysteresis curves for P(VDF-TrFE) copolymer samples with 72/28 mol% composition (tenth and fiftieth poling cycles) and (b) typical spatial polarization profile with the pressure step entering the sample at the electrode that was biased during poling.

Fig. 5. (a) Polarization- vs.-electric-field hysteresis curves for P(VDF-TrFE) copolymer samples with 75/25 mol% composition (tenth and fiftieth poling cycles) and (b) typical spatial polarization profile with the pressure step entering the sample at the electrode that was biased during poling.

IV. CONCLUSIONS

Commercial P(VDF-TrFE) copolymers with VDF/TrFE ratios of 50/50, 72/28 and 75/25 mol% were poled with the Bauer cyclical poling method where the samples have been subjected to 50 hysteresis cycles at an electric field of 80 MV/m, followed by additional 50 cycles at 100 MV/m. The PPSs method was used to investigate the uniformity of the polarization distribution across the sample thickness after poling for all three compositions, and the results were compared with the corresponding hysteresis loops. In addition, the ferroelectric sample properties were studied by calculating the β -phase content from FTIR measurements and by

measuring the dynamic piezoelectric d_{33} coefficients. Among the three compositions, the 75/25 mol% P(VDF-TrFE) films showed the highest remanent polarization values and d_{33} coefficients along with essentially uniform polarization distributions across the sample thickness – corresponding to the fact that the respective copolymer possessed the highest fraction of the polar β phase, which indicates that the TrFE content affects the uniformity of the polarization distribution. Though the hysteresis loops quickly saturate after 10 cycles for the 50/50 and 75/25 mol% compositions, the respective PPSs curves reveal a polarization distribution that is quite non-uniform across the sample thickness even after 50 cycles of poling at 100 MV/m. This suggests that a higher number of poling cycles might still be needed to achieve uniform polarization. The hysteresis behaviour of P(VDF-TrFE) films with 72/28 mol% which does not show a clear hysteresis saturation needs to be analysed further in order to understand the significant differences to the more optimal polymer films with the rather similar composition of 75/25 mol%.

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