Inhomogeneous distributions of polarization in polyvinylidene fluoride mono- and multilayer films studied by the laser intensity modulation method

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Abstract: The versatility of the laser intensity modulation method (LIMM) will be discussed concerning the interpretation of polarization distributions in multilayer films. Our LIMM equipment has been used to study monolayers, a bimorphic, and a four-layer film of PVDF. The growth of the polarization is measured in dependence on temperature for monolayer films. The poling dynamics is governed by thermally stimulated phase transitions and can be interpreted by an Arrhenius model. The LIMM capabilities and limitations are discussed for multilayer samples, including interfacial space charge effects between polarized and nonpolarized layers.

Key words: Distribution of polarization; multilayer films; polyvinylidene fluoride (PVDF)

1. Introduction

The discovery of the unique pyroelectric and piezoelectric properties of polyvinylidene fluoride (PVDF) [1, 2] started a large number of examinations on PVDF about 20 years ago, especially to understand the fundamental mechanisms of its interesting electrical properties. The essential influence on the macroscopic properties of PVDF of film preparation, stretching and poling under high electric DC-fields has been shown by using conventional methods like X-ray diffraction, IR-spectroscopy or the direct measurement of piezo- and pyroelectric coefficients. Unfortunately, all of these investigations yield results which are averaged across the polymer film. However Phelan et al. [3] demonstrated in 1974 the presence of an inhomogeneous polarization across the film by using frequency-dependent pyroelectric measurements.

These and results discussed by Marcus [4] have stimulated the development of various experimental methods to determine polarization and space charge distributions in polymer films, based either

on acoustical (pressure pulse [5—7] or pressure steps [8—10]) or thermal excitation of the sample layer [11—14] were the acoustical methods are connected with both better spatial resolution of the results and more extensive experimental requirements. Nevertheless, new developments in computational and experimental techniques enhanced the spatial resolution of calculated results obtained by using thermal waves and make them more attractive [15—18].

The purpose of this paper is the presentation of some aspects of a high resolution thermal wave method, the laser intensity modulation method (LIMM) developed by Lang and Das-Gupta [13], including the heat-transfer problem for multilayers, the discussion of the pyroelectric response together with the interpretation of some experimental results using our LIMM equipment.

2. Theory

LIMM is based on exposure of the surface of a dielectric film by a periodically modulated heat flux,

usually produced by a laser beam. The resulting variation of the surface temperature creates thermal waves that propagate into the sample volume and produce a definite local and time-dependent temperature variation. A pyroelectric current can be measured; it is caused by the interaction of the varying temperature with a polarization distribution $P(x)$ or space charge distribution $\rho(x)$. This $P(x)$ - or $\rho(x)$ -distribution can be determined from the relation between the modulation frequency $f = \omega/2\pi$ and the pyroelectric current amplitude $I(\omega)$ using a suitable deconvolution algorithm. Therefore the theoretical analysis of LMM consists of three main parts:

- I) the special heat conduction problem;
- II) the interaction between temperature profile and the polar properties of the dielectrics (pyroelectric effect); and
- III) the deconvolution technique.

2.1. Heat transfer problem

2.1.1. Homogeneous layer

We consider a planar sample of thickness L and assume L to be small compared to the lateral dimensions. So the relevant heat conduction equation has the following one-dimensional form

$$\rho_m c \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2}, \quad (1)$$

where t is the time, T the temperature difference from the ambient temperature T_0 , and x the spatial variable across the sample. The thermal properties of the sample are given by the density ρ_m , the specific heat c , and the thermal conductivity k , which are related to the thermal diffusion constant $K = k/\rho_m c$.

The heat transfer between the sample and its surroundings is assumed to consist of a time-dependent heat flux $q(L, t)$ at $x = L$ with

$$q(L, t) = q_0 \eta (1 + e^{i\omega t}), \quad (2)$$

where q_0 is the laser amplitude and η the absorptivity, and a heat loss at $x = 0$ and $x = L$ due to heat conduction, characterized by the heat transfer coef-

ficients h_0 and h_L , respectively. In our experimental equipment, freestanding polymeric layers are used and thus the parameters h_0 and h_L are equal. According to Lang and Das-Gupta [14] the temperature evolution can be separated into a transient T_u and a periodical T_ω component:

$$T = T_u + T_\omega. \quad (3)$$

By substitution of Eq. (3) into Eq. (1), we get an expression representing the transient and the periodical component of the heat-conduction problem. By separation of the variables each problem can be treated separately. This yields both the well-known plane-wall transient solution $T_u(x, t)$ [19] and the periodical solution $T_\omega(x, t)$ [14]

$$T_\omega(x, t) = \frac{(1 - i)q_0\eta \cosh[D(1 + i)x]}{2kD \sinh[D(1 + i)L]} e^{i\omega t}, \quad (4)$$

where $D = (\omega/2K)^{1/2}$. The term $\lambda = 1/D$ is usually called the thermal diffusion length at which a thermal wave of modulation frequency $\omega/2\pi$ is attenuated to $1/e$ of the initial amplitude.

The transient component, representing the averaged sample temperature at $t \rightarrow \infty$, yields a parabolic temperature profile. Hence, we can neglect the transient component in the following because only temporal changes of the temperature contribute to a periodic pyroelectric response, and we get from Eq. (4)

$$\frac{\partial T(x, \omega)}{\partial t} = (1 + i)\omega \frac{q_0\eta}{2kD} \frac{\cosh[D(1 + i)x]}{\sinh[D(1 + i)L]} e^{i\omega t}. \quad (5)$$

Equation (5) describes the spatial and temporal development of the temperature variation as a function of the modulation frequency. This relation allows the exact prediction of the thermal wave behavior through the sample if we know the constants q_0 , η , and the sample parameters L , K and k . This is demonstrated in Fig. 1 which shows the real part of the complex amplitude $\text{Re}\{\partial T(x, \omega)/\partial t\}$ as a function of the frequency according to Eq. (5).

All curves are normalized to 1 at the position $x = L$. The thermal diffusion length can be varied from $\lambda \approx L/10$ to $\lambda \approx L$ by variation of the frequency f between 10 Hz and 10 kHz, respectively (Fig. 1).

Fig. 1. Periodic component of the temperature $T_\omega(t)$ calculated for a sample with a heat flux defined by Eq. (2) and equal heat losses at both surfaces

2.1.2. Multilayer problems

From the point of view of heat transfer a multilayer consists of n adjacent single layers, each characterized by a local temperature distribution $T_i(x)$, thermal diffusivity K_i , and thickness L_i (Fig. 2).

Hence, the general multilayer problem can be represented by a system of n coupled differential equations

$$\frac{\partial T_i}{\partial t} = K_i \frac{\partial^2 T_i}{\partial x^2}, \quad (6)$$

$$(1 \leq i \leq n, L_{i-1} \leq x \leq L_i),$$

each describing the heat conducting process within the i^{th} layer. $2(n-1)$ boundary conditions are imposed due to the continuity of the temperature and the heat flux at the $n-1$ interfaces

$$T_i(L_i) = T_{i+1}(L_i), \quad (1 \leq i \leq n), \quad (7)$$

and

$$K_i \frac{\partial T_i}{\partial x} = K_{i+1} \frac{\partial T_{i+1}}{\partial x} \Big|_{L_i}, \quad (1 \leq i \leq n-1), \quad (8)$$

as well as two boundary conditions for the outer surfaces at $x = 0$ and $x = L_n$

$$K_1 \frac{\partial T_1}{\partial x} = h(T_1 - T_u) \Big|_{x=0}, \quad (9)$$

and

$$K_n \frac{\partial T_n}{\partial x} = \eta q_0(1 + \exp(i\omega t)) - h(T_n - T_u) \Big|_{x=L_n}. \quad (10)$$

We additionally use the n start conditions:

$$T_i(t = 0) = T_u, \quad (11)$$

assuming that the sample initially is at ambient temperature.

Three ways are proposed to obtain the solution $\{T_i(x, t)\}_1^n$. The exact analytical calculation of $T_i(x, t)$ can be carried out by solving the set of differential equations (Eqs. (6)–(11)) by a Laplace transformation, see for instance [19].

The temperature profile can be approximated by a constant temperature gradient $\Delta T_i / \Delta L_i$ within each layer if the individual layers are “thermally thin”. This condition mostly requires a partition of the original macroscopic layers into smaller sublayers. The advantage of the finite difference method compared to the analytical one is the conversion of the differential equations into linear difference equations [19]. Due to its numerical principle the finite difference method can be universally used, however, the convergence and numerical errors must be carefully considered. To explain the

Fig. 2. Thermal model of a multilayer system

third method we introduce new spatial variables $d\bar{x}_i = dx \cdot K_i^{-1/2}$ so that the heat conduction Eq. (8) becomes

$$\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial \bar{x}_i^2} . \quad (12)$$

Corresponding to the multilayer problem (Fig. 2), further new thickness parameters will be defined as

$$\bar{L}_i = L_i K_i^{-1/2} , \quad (13)$$

and

$$L = \sum_{i=1}^n \bar{L}_i = \sum_{i=1}^n L_i K_i^{-1/2} . \quad (14)$$

The temperature distribution within the multilayer can be directly obtained for all spatial positions $0 \leq \bar{x} \leq \bar{L}$ by substituting the variables $\bar{x}_i$ and $\bar{L}_i$ in Eq. (5). In a final procedure the calculated $T(\bar{x}, t)$ function must be transformed into the x -representation, e.g., by a numerical integration of the relation $dx = d\bar{x} \cdot K(\bar{x})^{1/2}$.

2.2. Pyroelectric response

According to Collins [20] both a spontaneous polarization $P(x)$ and a space charge distribution $\rho(x)$ can contribute to the frequency-dependent pyroelectric response. ΔV_0 is the total change of the potential difference across the dielectric sample, characterized by the thickness L and the permittivity ε . So the potential difference ΔV_p caused only by space charges is given by [21]

$$\Delta V_p = \frac{1}{\varepsilon \varepsilon_0} (a_L - a_\varepsilon) \int_0^L \rho(x) \int_0^x T(\xi, t) d\xi dx . \quad (15)$$

Here, $a_L = dx/LdT$ is the thermal expansion coefficient across the sample and $a_\varepsilon = d\varepsilon/\varepsilon dT$ is the temperature coefficient of the permittivity. The second contribution to ΔV_0 , caused by a permanent polarization, can be simply derived from the capacity of a capacitor containing a polarized dielectric

$$V_p = \frac{Q}{C} = \frac{PL}{\varepsilon \varepsilon_0} . \quad (16)$$

The total time derivation of Eq. (16) results in

$$\Delta V_p = \frac{PL}{\varepsilon \varepsilon_0} \left(\frac{1}{L} \frac{dx}{dT} - \frac{1}{\varepsilon} \frac{d\varepsilon}{dT} + \frac{1}{P} \frac{dP}{dT} \right) \Delta T . \quad (17)$$

The first two terms in Eq. (17) are related to a_L and a_ε , respectively. The third term $a_p = dP/PdT$ represents the pure dipolar pyroelectric effect without dimensional changes. The last component is normally attributed to a reversal change in crystallinity [22] and the temperature influence on the dipole amplitude across the sample [20]. Introducing in Eq. (16) an inhomogeneous temperature profile $T(x, t)$, we obtain

$$\Delta V_p = \frac{1}{\varepsilon \varepsilon_0} (a_p + a_L - a_\varepsilon) \int_0^L P(x) T(x, t) dx . \quad (18)$$

The alternating closed-circuit pyroelectric current $I_p(\omega)$ can be obtained by combination of Eq. (15) and Eq. (18) and the subsequent time differentiation gives

$$I_p(\omega) = \frac{A}{L} \left\{ (a_p + a_L - a_\varepsilon) \int_0^L P(x) \frac{\partial T}{\partial t}(x, \omega) dx + (a_L - a_\varepsilon) \int_0^L \rho(x) \cdot \int_0^x \frac{\partial T}{\partial t}(\xi, \omega) d\xi dx \right\} . \quad (19)$$

Integration by parts allows us to rewrite Eq. (19) as

$$I_p(\omega) = \frac{A}{L} \int_0^L \left[- (a_p + a_L - a_\varepsilon) \frac{dP(x)}{dx} + (a_L - a_\varepsilon) \rho(x) \right] \int_0^x \frac{\partial T}{\partial t}(\xi, \omega) d\xi dx . \quad (20)$$

There are two contributions $(a_p + a_L - a_\varepsilon)dP(x)/dx$ and $(a_L - a_\varepsilon)\rho(x)$ which independently can cause the resulting measurement response. It appears, therefore, impossible to distinguish a priori between space charge and polarization contributions in the measured total signal $I_p(\omega)$. One may tentatively carry out a deconvolution, assuming either a charge or polarization function. All experimental

results in this paper are discussed assuming a combined function called “effective polarization” $P_{\text{eff}}(x)$, nevertheless, the deconvoluted distribution will be interpreted depending on the physical background by polarization or space charge contributions.

2.3. Deconvolution algorithm

A set of $2 * N$ discrete measuring points $\{I_0, \omega\}_1^N$ and $\{I_L, \omega\}_1^N$ corresponding to a thermal excitation at the back and front electrode is used to determine the $P(x)$ - and/or $\rho(x)$ -function. One well-known method to solve the Fredholm integral equation (20) is to present the unknown polarization function $P_{\text{eff}}(x)$ as a truncated orthogonal polynomial series as described by Lang and Das-Gupta [14]. Another principle is based on the numerical integration of the discrete representation of Eq. (19). We can derive an expression for the complex amplitude of the pyroelectric current at the modulation frequency $\omega_j/2\pi$ by insertion of Eq. (5) into Eq. (18), and the replacement of the integral by a sum:

$$I_L(\omega_n) = \frac{Aq_0\eta\omega_j}{2kDL \sinh[D(1+i)L]} \cdot \left\{ (1+i)(a_p + a_L + a_e) \sum_{m1=1}^{M1} P(x_{m1}) \cdot \cosh[D(1+i)x_{m1}]x + \frac{1}{D} (a_L - a_e) \cdot \sum_{m2=1}^{M2} \rho(x_{m2}) \sinh[D(1+i)x_{m2}] \Delta x \right\}. \quad (21)$$

The analogous relation for the case of thermal excitation at the back surface ($x = 0$) can be obtained by replacing the spatial variable x by $L - x$.

Note that Eq. (21) contains information about both the amplitude of the measured quantity and its phase shift relative to the phase of the input heat flux. It can be shown that the projection of the complex signal onto an arbitrary phase $\Delta\phi$ contains the full information. The only exception is the case $\Delta\phi = 90^\circ$ where the average value of the polarization distribution is not represented by $I_p(\omega)$.

In our experiments, we have mainly measured the real part of the pyroelectric current $I_L^{\text{re}}(\omega_n)$ and $I_0^{\text{re}}(\omega_n)$. The corresponding relationship for a subsequent data processing was derived from Eq. (21):

$$I_L^{\text{re}}(\omega_n) = \frac{Aq_0\eta}{2kL} \left\{ (a_p + a_L - a_e) \cdot \sum_{m1=1}^{M1} B_{n,m1}^1 P_{m1}(x_{m1}) + (a_L - a_e) \cdot \sum_{m2=1}^{M2} B_{n,m2}^2 \rho_{m2}(x_{m2}) \right\}, \quad (22)$$

(for $n \leq N$) with

$$B_{n,m1}^1 = \frac{\omega_i \Delta x_{m1}}{D[1 + \cosh(2DL)]} \cdot (\cos(DL) \sinh(DL) [\cos(Dx) \cosh(Dx) - \sin(Dx) \sinh(Dx)] + \sin(DL) \cosh(DL) [\cos(Dx) \cosh(Dx) + \sin(Dx) \sinh(Dx)]) , \quad (23)$$

and

$$B_{n,m2}^2 = \frac{2K \Delta x_{m2}}{1 + \cosh(2DL)} (\cos(DL) \sinh(DL) \cdot \cos(Dx) \sinh(Dx) + \sin(DL) \cdot \cosh(DL) \sin(Dx) \cosh(Dx)) . \quad (24)$$

The restriction $n \leq N$ for the indices n in Eq. (22)–(24) is inevitable if we define a common input vector for all measured data points $I_L(\omega)$ ($1 \leq n \leq N$) and $I_0(\omega)$ ($N+1 \leq n \leq 2N$) corresponding to the front and back electrode irradiation

$$I = [I_L(\omega_1) \dots I_L(\omega_N), I_0(\omega_1) \dots I_0(\omega_N)]^T. \quad (25)$$

The coefficients $B_{n,m1}^1$ and $B_{n,m2}^2$ for $N+1 \leq n \leq 2N$ can be obtained from Eqs. (23) and (24) by an index exchange of m_1 by $M_1 - m_1 + 1$ and of m_2 by $M_2 - m_2 + 1$. Finally, the linear system of equations in matrix representation is

$$\begin{bmatrix} I \\ \vdots \\ I_{2N} \end{bmatrix} = C_1 \begin{bmatrix} B_{1,1}^1 & B_{1,2}^1 & \dots & B_{1,M1}^1 \\ \vdots & \vdots & & \vdots \\ B_{2N,1}^1 & B_{2N,2}^1 & \dots & B_{2N,M1}^1 \end{bmatrix} \cdot \begin{bmatrix} P_1(x_1) \\ \vdots \\ P_{M1}(x_{M1}) \end{bmatrix}^T \\
 \oplus C_2 \begin{bmatrix} B_{1,1}^2 & B_{1,2}^2 & \dots & B_{1,M2}^2 \\ \vdots & \vdots & & \vdots \\ B_{2N,1}^2 & B_{2N,2}^2 & \dots & B_{2N,M2}^2 \end{bmatrix} \\
 \cdot \begin{bmatrix} \rho_1(x_1) \\ \vdots \\ \rho_{M2}(x_{M2}) \end{bmatrix}^T, \quad (26)$$

or

$$I = \mathbb{B}F, \quad (27)$$

where the partial matrices $\mathbb{B}^1$ and $\mathbb{B}^2$ are combined into a matrix $\mathbb{B} = C_1 \mathbb{B}^1 \oplus C_2 \mathbb{B}^2$ and the vector F of the dimension $M_1 + M_2$ is defined by $F = [P, \rho]^T$. The constants C_1 and C_2 can be evaluated by comparison of Eq. (22) with Eq. (26). The normal solution of Eq. (27) is characterized by the pseudo inverse matrix $\mathbb{B}^+$

$$F = \mathbb{B}^+ I. \quad (28)$$

This Fredholm integral equation of the first kind leads to illconditioned normal equations which are very sensitive to numerical and experimental errors. Therefore, it is advantageous to use a least-square procedure modified by regularization [24] with the regularization coefficient γ

$$\|I - \mathbb{B}F\|^2 + \gamma \|F\|^2 \Rightarrow \text{Minimum}. \quad (29)$$

The matrix $\mathbb{B}$ can be written as $\mathbb{B} = \mathbb{U} \Sigma \mathbb{V}^T$, using the singular value decomposition (SVD) by Golub and Reinsch [25], where Σ is defined by

$$\Sigma = \mathbb{U}^T \mathbb{B} \mathbb{V} = \text{diag}(\sigma_1, \dots, \sigma_l) \in \mathbb{R}^{m,n}, \quad (30)$$

with

$$l := \min\{m, n\},$$

and

$$\sigma_1 \geq \sigma_2 \geq \dots \geq \sigma_r > 0,$$

$$\sigma_{r+1} = \sigma_{r+2} = \dots = \sigma_l = 0.$$

Here, Σ is a diagonal matrix with r nonzero diagonal elements. The regularized solution F_γ can be finally obtained by

$$F_\gamma = \mathbb{V}[\Sigma(\Sigma^2 + \gamma \mathbb{E})^{-1}] \mathbb{U}^T I. \quad (31)$$

This algorithm is the basis for handling the measured $I(\omega)$ -data (Fig. 3).

The measured current-frequency data set consists of logarithmically spaced $I_L(\omega)$ - and $I_0(\omega)$ -points in the frequency range from $f_u = 10$ Hz to $f_0 = 10$ kHz (Fig. 3 (1)). The subsequent deconvolution provides the polarization distribution, assuming a certain sample thickness L and thermal diffusivity K (Fig. 3 (2)). With this polarization distribution an "ideal current-frequency function" is calculated using Eq. (22) which is compared with the measured current-frequency function (Fig. 3 (3)).

The described procedure can be repeated partly or completely to study the influence of errors in the input sample parameters, e.g., a thickness error $\Delta L/L$. This is necessary due to the complex relationship between the measured quantities and the final distribution function. Hence, a number of simulations have been made [17] to estimate the influence of errors in L and K , at different noise levels superimposed with the $I(\omega)$ -data, as well as the ratio I_L/I_0 (caused by different absorptivities of both sample electrodes), and the shape of the polarization profile itself. It turns out that the most critical parameter is the regularization parameter γ , because the resulting vector F_γ strongly depends on the parameter γ for a given input vector I . The "best" value of the parameter γ cannot be derived from theory, hence a systematic parameter variation has been carried out. $\langle \Delta I \rangle = (I_i^{\text{mea}} - I_i^{\text{calc}})^2$ has been calculated (Fig. 4 (a–c)) as an objective measure to find out the optimum parameters were I_i^{mea} and I_i^{calc} are the measured and calculated values, respectively.

Figure 4 (a) demonstrates the interdependence of the thickness and thermal diffusivity. The valley depicted in Fig. 4 (a) is consistent with $K \propto L^{-1/2}$, corresponding to the heat conduction equation.

Figure 4 (b) shows a local minimum of $\langle \Delta I \rangle$ which indicates the independent influence of thermal diffusivity and the I_L/I_0 ratio on $\langle \Delta I \rangle$. Consequently, both parameters can be optimized independently with the help of the error criterion $\langle \Delta I \rangle$.

Fig. 3. Illustration of the algorithm to calculate the effective polarization $P_{\text{eff}}(x)$

Finally, the influence of the most difficult parameter γ is shown in Fig. 4 (c) combined with a variation of the assumed sample thickness. We do not find a two-dimensional local minimum as expected; we can only see a minimum for the thickness. Hence, it is necessary to define an upper limit for $\langle \Delta I \rangle$ to estimate the optimum regularization parameter γ .

3. Experimental

Figure 5 shows the schematic representation of the measurement equipment used for our LIMM measurements. A 50 mW He-Ne-laser provides a constant radiation flux which is modulated by a sinusoidally driven acousto-optical modulator (AOM).

Only the extraordinary output beam of the AOM is used because its intensity can be varied between nearly zero and about 40% of the input intensity. The beam irradiates the sample placed in a special sample chamber after passing some mirrors and lenses for guiding and focussing. Aluminum was evaporated onto both sides of the sample to obtain optically opaque electrodes and a high surface conductivity. An additional coating with black ink was applied to enhance the absorptivity. The sample itself has been clamped between two PMMA-rings with an inside diameter much larger than the pyroelectric active circular metallized area. This fact, as well as the use of very thin wires for electrical contacts guarantees the required thermal isolation expressed by a high thermal time constant τ_{th} .

The pyroelectric response is amplified by a current voltage converter which keeps to zero the electrical boundary condition (zero external field

Fig. 4. Two-dimensional representation of $\sum (I_i^{\text{mea}} - I_i^{\text{calc}})^2$ for the variation of:

- a) thickness and thermal diffusivity;
- b) thermal diffusivity and I_L/I_0 ratio;
- c) $\log(\gamma)$ and thickness

strength). A normal resistor R works as a current voltage converter. The condition $(RC_p)^{-1} \gg f_0$ must be fulfilled where C_p and f_0 denote the sample capacity and the highest modulation frequency. The application of an active current voltage converter is by all means necessary for an improved sensitivity of the electrical input circuit.

The small AC voltage is amplified by a broad band preamplifier UNIPAN 223-7 followed by a lock-in amplifier UNIPAN 233 processing the frequency range from 1 Hz to 150 kHz. Either the real or imaginary part of the amplitude of the complex pyroelectric response can be obtained depending on the phase shift $\Delta\phi$ relative to the reference signal generated by a digital controlled oscillator. The lock-in output voltage $U_p(\omega, \phi)$ will be transformed by an analog digital converter into a digital representation for further analysis. The equipment is fully controlled by a microcomputer. Use was made of a Turbo Pascal program for the data analysis, including deconvolution and graphics routines.

It should be noted that the LIMM does not provide the absolute values of the polarization and/or space charge distribution. This is due to uncertainty regarding the sample absorptivity, as well as the coefficients a_L , a_e , and a_p . Therefore, an additional measurement of the quasistatic (averaged) pyroelectric coefficient was used to calibrate the obtained polarization profiles. We will use the pyroelectric coefficient and the polarization in the same

Fig. 5. Schematic representation of the experimental equipment

meaning in the following because of the approximately linear relation between them in each kind of PVDF material.

4. Results and Discussion

The above-mentioned experimental procedure has been used in an extensive study of nonhomogeneous polarization effects in films of PVDF [17, 26], PA-6, PA-11 [18] and other polymeric materials. The poling behavior of all these materials has been investigated, i.e., the formation of a permanent macroscopic polarization within an high external field under definite poling conditions. Treatment of the polymer films usually at high temperatures initiates several processes in the polymeric solid, e.g., ferroelectric switching, conformational changes, field-induced transitions between crystalline modifications, and charge injection and transport phenomena. The semicrystalline polymers mentioned above exhibit similar poling effects regarding the spatial distribution, the magnitude, and dynamics of the pyroelectric effect. The following selected results on PVDF samples can therefore often be extrapolated to other polar polymer materials.

4.1. PVDF monolayers

4.1.1. Homogeneous polarized films

The LIMM procedure was first tested by use of the so-called completely polarized PVDF films [27] which are commercially available as “piezofilms” from several companies. In detail, we investigated two PVDF-foils (made by Solvay & Cie Bruxelles) which are known to be poled by a positive corona discharge [28]. The foils have a thickness of 25 and 9 μm , respectively, and are called S25bp and S9bp. Figure 6 shows the calculated polarization profiles. Both films show a relatively constant effective polarization within the sample, and an asymmetrically shaped polarization near the surfaces. Because of the highest experimental resolution of the LIMM in the surface region, we can consider this asymmetrical polarization decay as a real effect, caused by either structural inhomogeneities or an

Fig. 6. Polarization profiles of two Solvay-PVDF foils with a thickness of 25 μm and 9 μm for the samples S25bp and S9bp, respectively

asymmetrical electric field profile during the poling. Consequently, for this type of sample a spatial resolution of better than 0.5 μm is estimated. But it is a special property of the LIMM that the spatial resolution decreases from the surface to the central region.

4.1.2. Polarization dynamics

The LIMM was applied for systematic investigations on the temporal evolution of inhomogeneous polarization profiles. These measurements were made with mainly α -phase (nonpolar crystalline form II) containing PVDF-films at relatively weak poling field strengths ($E_p = 100 \text{ MVm}^{-1}$), where the appearance of inhomogeneous polarization distributions might be expected [27].

It is generally accepted that the presence of injected or intrinsic charges influences the formation of a permanent polarization in PVDF [8-10, 27, 29]. Eisenmenger and Haardt first described the interaction between space charges and dipolar polarization by a polarization dependent trap-model (TPP), assuming an enhanced trapping probability near polarized crystalline regions resulting in local charge compensating zones at the crystallite surfaces [8, 29]. Following this idea, Holdik and Bihler studied the temporal development of polarization profiles with in situ pressure pulse step technique (PPS) during poling at room temperature [9, 10, 27].

The present LIMM measurements have been made in order to study the influence of the poling temperature on the poling dynamics.

Sample preparation and characterization

The samples were weakly oriented, unstretched PVDF films made by Bamberg GmbH, FRG. The phase composition, consisting of both form-I (β -phase) and form-II (α -phase) fractions, was estimated by infrared spectroscopy [30] and presented a volume-ratio of 9:1 for the α phase relative to the β one. All 50- μm -thick films were metallized in vacuum with approximately 100-nm-thick aluminum electrodes on both sides (circles 4 mm in diameter). Samples were poled under controlled poling conditions E_p (poling field strength), T_p (poling temperature), and t_p (poling time). Each poling experiment was stopped after a definite poling time and the sample was investigated by LIMM in order to study the dynamics of polarization measurement procedure.

Poling dynamics at room temperature

The effective polarizations $P_{\text{eff}}(x)$ are shown in Fig. 7a for a series of PVDF samples poled at room temperature during various poling times.

Figure 7a shows asymmetric polarization profiles with a peak near the positive electrode. This behavior is either caused by different charge mobilities of positive and negative charge carriers, or by asymmetric charge injection from the electrodes corresponding to the TPP model.

The maximum pyroelectric coefficient value is (35–40) $\mu\text{Cm}^{-2} \text{K}^{-1}$ for pure β -PVDF films, indicating a contribution of about (3.5–4.0) $\mu\text{Cm}^{-2} \text{K}^{-1}$ to the pyroelectricity [17] by the initial β part of the material used. In fact, the poling profiles could be interpreted up to 60 s as being only caused by ferroelectric switching of the β phase. Above this temporal interval the positive polarization peak increases slower and obtains its final state after nearly 3000 s. This "long time process" can be attributed to the field induced $\alpha \rightarrow \delta$ phase transition, which needs higher electrical field strengths. Consequently, a transition of the modification is supposed to be only restricted to the anode region.

a

b

c

Fig. 7. Effective polarization $P_{\text{eff}}(x)$ of a 50- μm -thick PVDF sample in dependence on the poling time t .

Poling field strength: $E_p = 1 \text{ MVcm}^{-1}$;

Poling temperatures: a) $T_p = 20^\circ\text{C}$

b) $T_p = 60^\circ\text{C}$

c) $T_p = 80^\circ\text{C}$

Poling dynamics of thermally poled PVDF films

Figure 7b shows the polarization profiles obtained at a poling temperature of $T_p = 60^\circ\text{C}$. The results show a drastically accelerated temporal development of the polarization, as well as a general increase of maximum pyroelectric activity up to $30 \mu\text{Cm}^{-2} \text{K}^{-1}$. The steady-state situation was reached after a few seconds, indicating a very quick formation of a large fraction of polar phase. The expected increase of the β phase volume fraction could not be confirmed by using infrared spectroscopy, thus the observed enhancement of poling efficiency can only be attributed to the $\alpha \rightarrow \delta$ transformation.

Additional PVDF series, poled at $T_p = 80^\circ\text{C}$, confirm this tendency and show a similar picture to that discussed above (Fig. 7c). In addition, a further increase in pyroelectric maximum values of about 10–20% indicates the appearance of high field $\alpha \rightarrow \beta$ conformational transitions.

Quantitative interpretation of poling dynamics

It is remarkable that the time for reaching the final polarization profile decreases from about 3000 s at $T_p = 25^\circ\text{C}$ to a few seconds already at $T_p = 60^\circ\text{C}$. It was attempted to explain this immense temporal acceleration on the basis of a thermally activated process. We estimated an activation energy of $E_a \cong 2 \text{ eV}$, assuming an Arrhenius type behavior:

$$t_p(T) = t_0 \exp\left(\frac{E_a}{kT}\right), \quad (32)$$

where t_0 and E_a are the preexponential factor and the activation energy, respectively. Both the dynamics of the various dipolar switching processes itself and the transport of real charges into the polarized regions could contribute to the resulting poling dynamics, including its temperature behavior in accordance with the TPP-model [27]. But the pure electrical conduction in PVDF films is usually characterized by an activation energy of about 1 eV [27, 31]. Therefore, some results from the literature has been fitted to a simple model proposed by Furukawa et al. [32]:

$$P(t) = P_0 \left(1 - \exp\left[-\frac{t}{t_s}\right]\right), \quad (33)$$

in order to decide whether the conduction or the switching processes are dominant with respect to the temperature dependence of the poling behavior. Here, $P(t)$ represents the time-dependent volume fraction of the polar phase, following the switching process induced by the electrical field characterized by an averaged switching time t_s and the critical field strength E_k :

$$t_s = t_{s0} \exp\left[-\frac{E}{E_k}\right]. \quad (34)$$

A relation between the three main poling parameters E_p , t_p , and T_p can be derived by combination of Eqs. (34) and (35) with the Arrhenius approach of Eq. (32). We determined some different values of the activation energy for these elementary processes, assuming the description of the ferroelectric switching of the β phase, as well as of the field-induced modification transitions $\alpha \rightarrow \delta$ or $\alpha \rightarrow \beta$ by the same model. Hence, we obtained, e.g., $E_a = (0.5\text{--}0.6) \text{ eV}$ for the ferroelectric switching at temperatures from -60°C to 20°C [32], and $E_a = 0.2 \text{ eV}$ for the high field $\alpha \rightarrow \beta$ conformational transition at higher temperatures by using experimental data from the literature [33]. However, these results indicate that the temperature dependence of the poling dynamics is mainly influenced by the thermal activation of the charge transport. On the other hand, the high activation energy obtained for the entire poling dynamics cannot be explained by a normal superposition of the mentioned elementary phenomena, but rather by accepting a positive feedback mechanism in accordance to the TPP model.

3.2. PVDF multilayers

The following results were obtained from PVDF multilayer samples of prepolarized PVDF films S25bp and S9bp, and 25- μm -thick nonpolarized PVDF material S25bu. The films were glued to each other with a two-component epoxy resin that formed about 5- μm nonpolar interface layers between the PVDF films. Both surfaces of the obtained PVDF stacks were metallized under vacuum conditions.

Using this procedure a variety of multilayers were prepared consisting of two, three or four layers in different arrangements with respect to the polarization state and polarization direction.

The obtained films were studied for two main reasons:

- to find out the LIMM capabilities and limitations for multilayer samples, and
- to study the interfacial space charge effects between polarized and nonpolarized PVDF-films.

Combination of polarized and nonpolarized films

The theoretical polarization profile of an ideal asymmetric monomorphous layer is shown in Fig. 8a. Whereas the left part of the profile can be attributed to the polarized layer, the right part exhibits no

polarization. The complete deconvolution procedure was tested with an ideal polarization distribution $P(x)$ and relevant sample parameters in order to investigate the influence of numerically caused deviations, for instance. The recalculated polarization functions are presented in Fig. 8a for two different regularization parameters γ together with the original $P(x)$ function. The tendency towards a nearly perfect reproducibility of the polarization distribution in the surface layer is easily recognized, whereas the details in the middle of the layer cannot be reproduced correctly. An analogue analysis can be seen for the combination of two polarized layers in series in Fig. 8c.

The observed negative part of the from measured data polarization profile measured data calculated

Fig. 8. Polarization profiles of bimorphic films.
One polarized and one unpolarized layer: a) model calculations;
b) experimental result.
Two polarized layers in series: c) model calculations;
d) experimental results

(Fig. 8b) indicates a significant pyroelectric activity in the nonpoled layer which cannot originate from a permanent polarization. Spatially distributed space charges $\rho(x)$ can also contribute to the pyroelectric signal according to Eq. (20). The surface charges σ_{PO} and σ_{PL} induced by polarization compensate the polarization-caused electrical field to zero if the polarization is constant within the sample [14].

The charge distribution becomes much more complicated in the case of multilayers. Starting with totally or partially charge-compensated polarized single layers in preparing the multilayer sample, we obtain additional layers where a part of the compensation charges will be localized. In detail, one interlayer of adhesive causes two charge layers located near the polymer-resin interface.

In order to discuss an internal field distribution proportional to the induced polarization, we made the following assumptions:

- i) all polarized single layers are equally and homogeneously polarized;
- ii) the polarization of each single layer is compensated by a discrete surface charge layer (also called "local compensation"), and
- iii) the degree of compensation can vary from 0% (no compensation) to 100% (total compensation).

The case of completely locally compensated polarization does not yield an internal field by an induced polarization. However, the compensation charges reduce the total pyroelectric effect to the dipolar component a_p , as discussed by Collins [20]. In consequence, an incomplete charge compensation of the polarized PVDF layer corresponding to Fig. 8a should result both in a higher pyroelectricity in the polarized (left) layer, and in a negative pyroelectric activity in the unpoled (right) part of the sample. In fact, the experimentally obtained curve in Fig. 8b confirms the assumed incomplete local charge compensation.

The polarization distribution of a bilayer with two polarized PVDF films in series (Fig. 8d) exhibits a gap in the pyroelectric profile which is significantly deeper than expected (Fig. 8c). Considering the limited experimental resolution in the middle of the layer the observed minimum requires the presence of a strong negative pyroelectric activity in the central region. This effect is in agreement with the internal field distribution which corresponds to a low

degree of local charge compensation ($<50\%$). A probable explanation for this effect may be the partial neutralization of the expected double layer of the compensation charges in their own electric field within the adhesive layer.

Four-layer films

Figure 9 shows the polarization profile of a multilayer consisting of four 9- μm -thick polarized PVDF films. The direction of the polarization is given at the top of Fig. 9. The polarization profile of this four-layer film can be represented by $+0+0-0-$, where 0 is the adhesive layer. The polarization profile could be resolved principally by LIMM. Only the thickness of the layers is not equally reproduced due to the inhomogeneous spatial resolution, as discussed before. However, there is a remarkable difference in the pyroelectric activity between the left (positive) and the right (negative) parts of the sample. The four-layer sample can be interpreted as a sandwich of two oppositely directed bimorphic samples in analogy with the described effects at the symmetric bimorphic layer (Fig. 8b).

Both the differences in peak heights and depths of the minima seem to indicate a corresponding different degree of local charge compensation in the bimorphic layers (at about 8 μm and 32 μm). Conse-

Fig. 9. Experimental polarization profile of a four-layer film

quently, the right bimorphic layer may exhibit a lower charge density at its interfaces relative to the left one. A probable reason for this difference might be variations in the electrical conductivity of these interlayers, for instance, caused by a different thickness or chemical composition of the epoxy resin.

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Discussion

WENDORFF:

What about using blocked electrodes to distinguish between space charge effects and dipolar effects?

WÜNSCHE:

The comparison of LIMM results with and without blocking electrodes can give some hints for the relative contributions of charge trapping and dipoles, but the effect of blocked electrodes was not investigated. We have only used aluminum as electrode material up to now.

KREMER:

What limits the spatial resolution of the Laser Intensity Modulation Method (LIMM)?

WÜNSCHE:

The resolution increases in the surface region with increasing frequency, whereas the resolution remains nearly constant in the center of the film. A resolution of about 0.5 μm can be reached near the surface with frequencies up to 10 kHz.

KILIAN:

Could you comment on the influence of the structure on your results?

WÜNSCHE:

Time behavior and attainable absolute values of the polarization are strongly influenced by the content of α -

and β - phase in the investigated PVDF films. Additionally, the calculated polarization peaks may be caused by structural phenomena near the layer surface, but this must be investigated by additional experiments.

KREMER:

What is the degree of trapping of the mobile charge car-

rier considered in the evaluation of the measured currents?

WÜNSCHE:

The combination of thermally stimulated currents, with its conclusions concerning the distribution of the activation energy, and LMM seems to open a possibility to estimate the relative contributions caused by trapped charges or dipoles, respectively.