

RESONANCE CHARACTERISTICS AND POLARIZATION PROFILE OF
PARTIALLY POLED P(VDF-TrFE) COPOLYMERBernd PLOSS¹, H.L.W. CHAN², K.W. KWOK², and C.L. CHOY²¹Institut für angewandte Physik, Universität Karlsruhe,
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Thick films of polyvinylidene fluoride/trifluoroethylene (P(VDF-TrFE)) copolymer with the composition 80/20 mol-% were poled at elevated temperature. The dielectric spectrum of this film shows two resonance peaks which correspond to the fundamental and second harmonic of the thickness vibration mode. Even harmonics of the thickness mode are usually not observed as they are not coupled to the electrical excitation. Piezoelectric and pyroelectric profiling experiments using both the pressure wave propagation (PWP) method and the laser intensity modulation method (LIMM) show that the copolymer has an inhomogeneous polarization profile which leads to the observed second order harmonic. In particular, these methods indicate that an unpoled region exists near the cathode side of the sample. By fitting the observed dielectric spectrum to a model of two Lorentz oscillators, the oscillation strengths have been estimated and found to be consistent with those obtained from the appropriate Fourier coefficients of the measured pyroelectric profile.

1. Introduction

Because of their reasonably high electromechanical coupling factors and acoustic impedance appropriate for efficient acoustic coupling to water, vinylidene fluoride/trifluoroethylene copolymers are promising materials for transducer applications. For efficient excitation of thickness vibrations in the MHz range, films with thicknesses in the millimeter range are required. The recent observation that films prepared under particular poling conditions show a resonance at the second harmonic of the thickness vibration [1] provides the motivation to study the relation between the resonance characteristics and the polarization profile.

2. Sample preparation and poling

The starting material for the samples was 800 μm thick extruded vinylidene fluoride/trifluoroethylene copolymer in the composition 80/20 mol-% supplied by Atochem North America Inc.. Appropriately poled copolymer of this VDF content was reported

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to have the highest thickness electromechanical coupling factor amongst copolymers of different compositions [2]. The sample was first annealed at 120 °C for five hours. Metallized on both sides with silver paint, the sample was thermally poled at 105 °C for five hours. The electric voltage applied to the samples was about 21 kV which corresponds to a mean electric field of 26 MV/m. For the LIMM investigations a circular shaped sample with a diameter of 8 mm has been punched out of the thick film.

3. Resonance characteristics

The sample impedance has been recorded as a function of frequency between 500 kHz and 4 MHz. The real and imaginary part of the relative permittivity (ϵ' and ϵ'') calculated from the measured impedance are shown in Figure 1. A major resonance is seen at about 1.3 MHz which corresponds to the fundamental thickness vibration mode. With a sound velocity $v \approx 2280$ m/s the sample thickness $d = 800$ μm corresponds to half the wavelength of the sound wave at a frequency $f \approx 1.4$ MHz. The permittivity spectrum shows a second resonance at 2.6 MHz corresponding to the second harmonic of the thickness vibration mode. Usually, even number harmonics of the thickness mode are not observed in piezoelectric plates or films as they are not coupled to the electrical excitation. The measured permittivity spectrum has been fitted to the sum of two Lorentz oscillator functions

$$\epsilon(\omega) = \sum_{k=1}^2 \frac{\omega_k^2 \Delta\epsilon_k}{\omega_k^2 - \omega^2 - i\gamma_k\omega} \quad (1)$$

where the parameters are given in the following table:

k	$f_k = \omega_k/2\pi$	$\Delta\epsilon_k$	γ_k/ω_k
1	$1.29 \cdot 10^6$	0.125	0.08
2	$2.60 \cdot 10^6$	0.045	0.08

As shown in Figure 1, the theoretical curves fit precisely the two observed resonances. In addition, the measured permittivity spectrum shows a slight decrease of ϵ_1 proportional to $1/f$ and a dielectric loss independent of frequency. From the fitted results the ratio of the oscillator strengths of the second harmonic and the fundamental thickness vibration $\Delta\epsilon_2/\Delta\epsilon_1 = 0.36$. To investigate whether the piezoelectric excitation of the second harmonic thickness vibration is caused by the non-uniform polarization profile in the sample, experiments have been performed using the pressure wave propagation (PWP) method and the pyroelectric laser intensity modulation method (LIMM).

4. Piezoelectric profiling

The pressure wave propagation method [3,4] has been used for profiling the piezoelectric coefficient in the thickness direction of the sample. Laser pulses from a Spectral Physics Nd/YAG laser are absorbed by the graphite coating on one electrode of the sample. A pressure pulse is generated due to ablation and propagates along the thickness direction of

the sample with the velocity of sound. The setup is described in more detail in [5]. By an appropriate change of the target the bipolar pressure pulse which was observed in earlier experiments disappeared and only a positive or a negative pulse was observed. Figure 2 shows the signals as functions of time. In the upper and lower graphs the light pulse hits the sample electrode at the anode side and the cathode side, respectively. (Anode is the side connected to positive voltage and cathode is the side connected to ground during the poling process.) The time-axis in the lower graph is drawn in the negative x direction to facilitate the comparison of both graphs. Time $t = 0$ is when the pressure pulse enters the sample. The results of the PWP investigations clearly indicate an unpoled region of thickness about $250 \mu\text{m}$ at the cathode side of the sample.

5. Pyroelectric profiling

To record the profile of the pyroelectric coefficient, the laser intensity modulation method [6] with the experimental equipment as described in [7] has been used. The sample is periodically heated at one electrode by the sinusoidally intensity modulated light of a laser diode with a power of 10 mW. A thermal wave is generated at the sample surface which propagates in the thickness direction of the sample. The decay length of the thermal wave is determined by the thermal diffusivity $D = 6.1 \times 10^{-8} \text{ m}^2/\text{s}$ of the copolymer and the modulation frequency f . The amplitude and phase of the pyroelectric current are recorded as functions of f . For a $800 \mu\text{m}$ thick P(VDF-TrFE) sample the spectra of the pyroelectric current have to be recorded down to $f \approx 30 \text{ mHz}$. To avoid heat loss from the sample to the surroundings and to realize a one-dimensional propagation of heat in the sample, it had been attached to the sample holder only by thin wires at the electrode surfaces. The measurements were performed in vacuum. To avoid the influence of the heat capacity of the electrodes, the silver paint had been replaced by 800 nm thick evaporated silver films. The measured pyroelectric current spectra for heating at the anode and at the cathode electrode are shown in Figure 3 and Figure 4, respectively. According to the method given in [8] the pyroelectric distribution has been calculated from the 45° out-of-phase component of the measured spectra. The obtained pyroelectric profile shows a $\approx 180 \mu\text{m}$ thick nearly unpolarized region at the cathode side. The pyroelectric profile even indicates a small inversely oriented polarization in this region. At the anode side only a $5 \mu\text{m}$ thick unpolarized region is detected. In addition, the pyroelectric profile shows a step-like structure in a depth of $200 \mu\text{m}$ from the anode side.

For a comparison with the resonance characteristics the first and second order Fourier components \mathcal{F}_1 and \mathcal{F}_2 have been evaluated from the pyroelectric profile in Figure 5 using the following expression:

$$\mathcal{F}_k = \int_0^d p(x) \sin(k\pi x/d) dx \quad (2)$$

The resulting ratio is $\mathcal{F}_2/\mathcal{F}_1 = 0.34$. This value is nearly equal to the ratio of the oscillator strengths of the second harmonic and the fundamental thickness vibration $\Delta\epsilon_2/\Delta\epsilon_1 = 0.36$ as given in section 3.

6. Discussion and Conclusion

The results obtained using the PWP and L IMM techniques show that the polarization in the sample is not uniform. A non-polarized region N near the cathode side of the sample is detected by both methods. $N \approx 250 \mu\text{m}$ from PWP measurement and $N \approx 180 \mu\text{m}$ from L IMM result. The difference may be caused by the preparation of the sample for the L IMM measurement, the punching and the evaporation of silver electrode may have affected the polarization distribution in the sample. As the sample was reduced to 8 mm in diameter, it is not possible to repeat the PWP measurement after the L IMM measurement. The presence of a non-polarized region near the cathode indicates that negative charge is injected into the sample from the cathode during the poling procedure, consistent with the results in [9]. The injected space charge leads to a non-uniform profile of the electric field in the course of poling. Near the cathode side the electric field is partially shielded, hence in this part of the sample the coercive field is not reached. The studies of resonance characteristics and pyroelectric profile clearly show that a non-uniform polarisation profile is the reason for the piezoelectric excitation of the second harmonic of the thickness vibration mode. The oscillator strength of the second harmonic relative to that of the fundamental mode is in quantitative agreement with the appropriate Fourier components of the pyroelectric profile.

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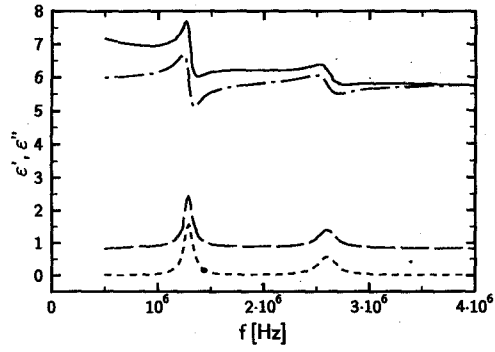


FIGURE 1 Real part ϵ' and imaginary part ϵ'' of the permittivity as functions of frequency f . Data (—, ---) and fit with a sum of two Lorentz oscillator functions (-·-·-, ····).

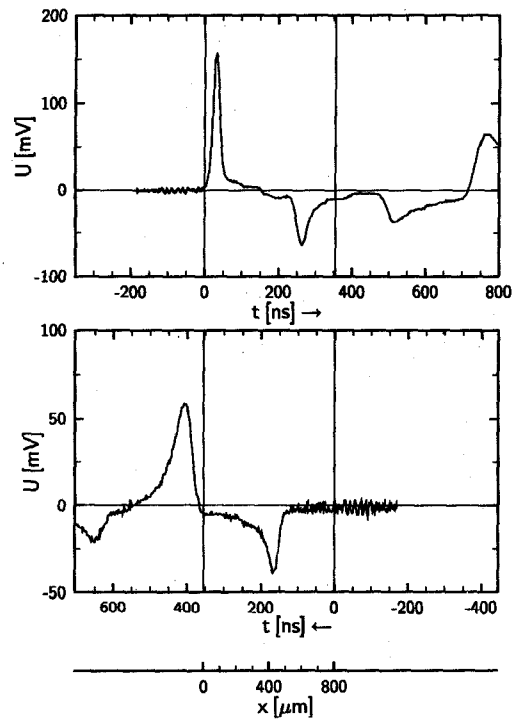


FIGURE 2 Pressure pulse propagation response of the partially poled P(VDF-TrFE) film for an excitation at the anode side (upper graph) and at the cathode side of the sample (lower graph). The time-axis in the lower graph is drawn in the negative x -direction to facilitate the comparison of both graphs. The pressure pulse enters the sample at $t = 0$.

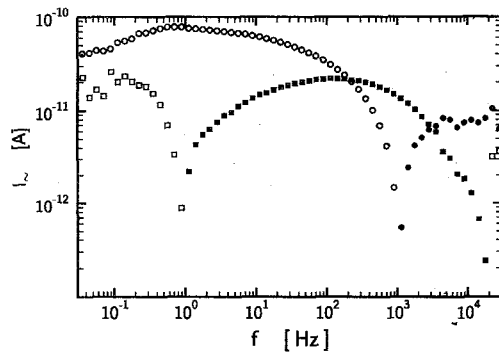


FIGURE 3

The measured pyroelectric current spectrum for the thermal excitation at the anode side of the sample as a function of modulation frequency f . Symbols used: real part > 0 : \circ , real part < 0 : \bullet , imaginary part > 0 : \square , imaginary part < 0 : \blacksquare .

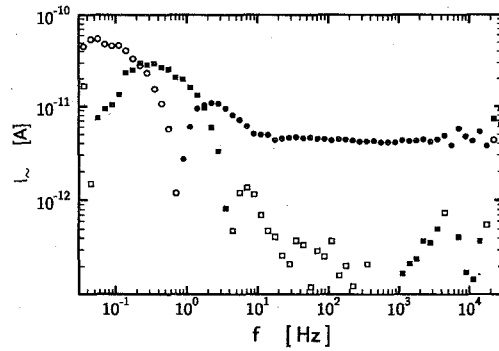


FIGURE 4

The measured pyroelectric current spectrum for the thermal excitation at the cathode side of the sample as a function of modulation frequency f . Symbols as in Figure 3.

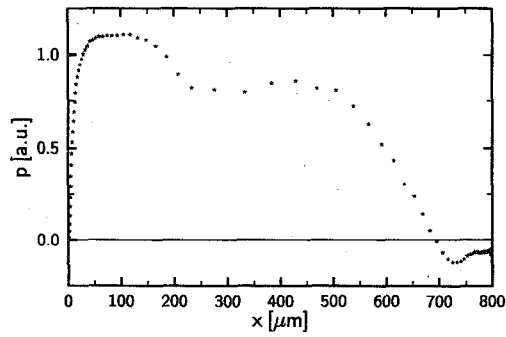


FIGURE 5

The spatial profile of the pyroelectric coefficient p as a function of the depth x , calculated from the measured spectra in Figures 3 and 4.