THERMAL WAVE METHODS: SOME EXPERIMENTAL PITFALLS.

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Abstract

Uncertainties in the spatial distributions calculated from thermal wave data are normally attributed to the ill-posed deconvolution problem. This paper focusses on the impact of "ill-posed" experimental conditions on the pyroelectric spectra. The spectra are affected by structural inhomogeneities and temporal changes in the electrical and thermal properties, by distortions caused by the electric circuit, by frequency-dependent properties and by piezoelectricity. Experimental results are given for PVDF and LiTaO₃. Suggestions are made to reduce the effect of experimental errors.

1. Introduction

Polarization and space charge distributions in electret films are frequently determined by means of thermal wave techniques rather than with the more elaborated piezoelectrically-based acoustical techniques. The thermal techniques apply either heat pulses [1] or continuous waves [2] and are attractive because of their moderately priced equipment and their high spatial resolution. Since the transient and cw technique are basically equivalent, we restrict ourselves to the laser-intensity modulated, cw-method (LIMM) developed by Lang and Das-Gupta [2].

LIMM has undergone gradual improvements regarding reliability and achievable resolution owing to the use of advanced numerical deconvolution procedures (singular value decomposition, regularization techniques, etc. [3-5]). The prominent features of LIMM have been demonstrated for simulated and for measured data [3, 6, 7]. The reproducibility of nearly homogeneously polarized samples is always satisfying, whereas for nonhomogeneous distributions the predictions and the outcome of LIMM is less satisfactory.

In order to obtain well-defined nonuniform properties we have used two types of model samples; one consisted of a bimorph of oppositely poled PVDF films, the other was made from poled PVDF and of LiTaO₃, both provided with a thick paint layer. Their pyro-response allowed us to obtain a quantitative idea of the impact of possible errors on LIMM spectra.

2. Overview of effects on LIMM-spectra

2.1 Limitations of the electrical and thermal model

For a pyroelectric film of thickness L and area A , containing a nonuniform polarization $\vec{P} + P(x)$ and a space charge distribution $\rho(x)$, the LIMM-current $I_L(\omega)$ reads [3]:

$$I_-(\omega) = \alpha_p A P \frac{dT(\omega)}{dt} + \frac{A}{L} (\alpha_p + \alpha_L - \alpha_\epsilon) \int_0^L P(x) \frac{\partial T(x, \omega)}{\partial t} dx + \frac{A}{L} (\alpha_L - \alpha_\epsilon) \int_0^L \rho(x) \int_0^x \left[\frac{\partial T(x', \omega)}{\partial t} - \frac{dT(\omega)}{dt} \right] dx' dx \quad (1)$$

where α_p , α_L and α_ϵ denote the temperature coefficients of the polarization, the thickness and the permittivity, respectively. For convenience we have considered only the 1st and 2nd term due to the permanent polarisation $P + P(x)$ in our model calculations. Eq.1 can easily be extended to multi-layers provided that each layer is homogeneous.

On the other hand an x-dependent thermal expansion $\alpha_L(x)$, permittivity $\epsilon(x)$ or $\alpha_\epsilon(x)$ require a more general expression given in [8]. The consideration of position-dependent properties is a prerequisite in the analysis of LIMM-spectra of multilayers, such as laminates of different polymers, coatings on pyroelectric sensors etc. Such an analysis is still straightforward if all layers have space-independent properties. However, a LIMM-analysis is not feasible if the material properties are spatially distributed in an unknown way.

Structural gradients in properties can e.g. be caused by differences in the degree of crystallinity. As a consequence, dielectric or thermal anisotropies appear near the surface, where LIMM possesses its highest resolution.

2.2 Frequency-dependent dielectric properties

The permittivity will affect the pyroelectric spectrum of multi-layers if each layer has different frequency-dependent dielectric constants $\epsilon(\omega)$. But, also LIMM-measurements on monolayers might suffer from dielectric relaxations, via the term $\alpha_\epsilon(\omega, T) = d \ln \epsilon'(\omega, T) / dT$. This term can be related to the dielectric losses by the approximation [9]

$$\alpha_\epsilon(\omega, T) = \frac{\partial \ln \epsilon'(\omega, T)}{\partial T} \approx \frac{2E_A}{\pi R T^2} \cdot \frac{\epsilon''(\omega, T)}{\epsilon'(\omega, T)} \quad (2)$$

where E_A is the activation energy at the temperature T , and ϵ' , ϵ'' and R denote the real and imaginary part of the permittivity and the gas-constant respectively. Strong relaxation processes - like the glass transition - may lead to rather high values ($> 10^2$) of the term α_ϵ (cf. Fig.3).

2.3 Bending and tensile piezoelectricity

The one-sided LIMM-heating causes an asymmetric expansion, which in a free film results in a deformation. In films having an inhomogeneous polarization this deformation causes in return a piezo-electric response [10, 11]. Bending resonances (flexural waves) are visible in many published LIMM-spectra. The fundamental frequency f_r depends on the film width b , the thickness L and the transverse sound velocity v_t and occurs in PVDF-films at around 1kHz:

$$f_r = \frac{9}{32} \frac{\pi L v_t}{b^2} \quad (3)$$

The thermally generated deformations give also rise to a nonresonant piezo-contribution in PVDF, which might reach 20% of the pyro-current at high frequencies. The dimensions, the elastic properties and the way of fixing the pyroelectric sample are therefore all essential.

2.4 Characteristics of the electronic circuit

The electronics of a LIMM-set-up includes 3 main components:

- i) modulation driver (e.g. for an acousto-optic-modulator)
- ii) preamplifier, usually a current- to- voltage converter, and
- iii) gain-phase analyzer, e.g. lock-in amplifier or frequency-response analyzer.

The errors resulting from the electronic parts arise from the limited bandwidth of the gain/phase measurement, noise and interference between driving voltage and input circuit. All these error sources become the more important the higher the operation frequency (> 1 kHz).

The gain/phase characteristics of the preamplifier often form the crucial factor. They depend on the gain, filter time constants, capacitive load, and modulation level. Our lock-in amplifier on the other hand had an excellent gain/phase behaviour throughout the whole frequency range from 0.001 Hz to 100 kHz.

We have corrected all the LIMM-spectra measured by performing a calibration with a fast photodiode (cut-off frequency 100MHz, capacitance < 10 pF); for each sample such a correction is crucial.

2.5 Temporal influences

Drift of the laser intensity, degradation of the heat absorbing layer or temporal changes in the polarization due to depolarization processes or charge relaxations in PVDF-films may also affect the LIMM-spectrum. One way to visualize temporal effects is the use of a random frequency scan rather than a sequential one.

A summary of the impact of the various processes that can alter the LIMM-spectrum is given in Fig.1.

Fig.1 Survey of possible distortions of a LIMM-spectrum.

3. Experiments

3.1 Experimental set-up

The equipment used for LIMM is described in detail in [12]. A He-Ne-laser combined with an acousto-optic modulator provides the intensity modulated radiation (< 5 mW r.m.s). The sample is placed in a holder either under atmospheric pressure or in vacuum. The pyroelectric current was converted by a current amplifier (Keithley, model 428) to an ac-voltage, and was analyzed by a digital signal processing lock-in amplifier (Stanford Research System, SR850).

The dielectric measurements were performed over a wide frequency range (10^3 Hz

to 10^6 Hz) by means of an LCR-meter (HP 4284A) and a low-frequency system consisting of an electrometer (TNO) and a frequency response analyzer (Schlumberger, model 1260). Films of PVDF were investigated from -150 to 250°C in a nitrogen-gas heated cryostat.

The device programming and data acquisition were computer controlled.

3.2 Dielectric studies on PVDF-films

Dielectric measurements were performed on 2 biaxially stretched PVDF films (Solvay, S9bp - 9 μ m, Kynar, K30bp - 30 μ m), and on 1 isotropic film (Bamberg, B50uu - 50 μ m). The real part of the permittivity for isotropic PVDF is given in Fig. 2.

Fig.2 Frequency dependence of ϵ' of isotropic PVDF (>90% α -phase) at various temperatures around 25°C (0, 5, ... 40°C).

Fig.3 Frequency dependence of $\alpha_t = d \ln \epsilon' / dT$ for 2 poled, stretched PVDF films at 25°C. In addition, the influence of the temperature (20 to 30°C) on α_t is shown for isotropic PVDF.

Fig.3 shows that the frequency dependence of the temperature coefficient α_t differs markedly for the biaxially stretched and the isotropic PVDF films. The high frequency upswing in α_t is due to the influence of the glass-transition, while the low-frequency increase for isotropic PVDF is caused by the mid-temperature relaxation of the α -phase.

To illustrate the effect of a frequency-dependent α_t on the LIMM-spectrum of a nonuniformly polarized sample we have calculated the pyro-response of a bimorph of oppositely poled PVDF of 9 μ m with eqn.(1) using the α_t -data from Fig.3 and the parameters $\alpha_t = 2 \cdot 10^{-4} \text{K}^{-1}$ and $\alpha_p = -4 \cdot 10^{-4} \text{K}^{-1}$.

We see that up to $4 \cdot 10^3$ Hz biaxially stretched PVDF is scarcely affected by dielectric relaxations, whereas the LIMM spectrum of isotropic PVDF clearly is.

3.3 Piezoelectric effects

To estimate the contribution of piezoelectricity to the LIMM-response we have investigated mono- and bilayers of PVDF and LiTaO₃.

Fig.5 shows the LIMM-spectrum of 20x10 mm² biaxially stretched PVDF-film (Solvay, L=40μm) for different mechanical fixations. The samples were coated with a 20μm thick black paint which served both as heat absorber and as electrically neutral layer.

Surprisingly, no curve approaches the expected zero current level at high frequencies, when the thermal waves cannot reach the pyroactive PVDF-layer anymore. Obviously, this high-frequency response must originate from a thermoelastically generated (negative) piezocurrent.

Fig.4 Calculated LIMM-spectra for a bimorph consisting of oppositely poled PVDF films. The solid curve corresponds to a constant $\alpha_c = 3 \cdot 10^{-3} \text{K}^{-1}$, while the other curves are calculated using the actual α_c -data of Fig.3.

Fig.5 LIMM-spectra of PVDF coated with a 20μm black paint in order to reveal the contribution of piezoelectricity. Results for different mechanical fixations are shown: pre-bended, 0% strain, 13% strain and backed with PS-foam.

Fig.6 LIMM-spectra of the same PVDF sample, but now coated with 1 mm epoxy on the back side as a function of the degree of cure.

For more clarity, the curves have been displayed by 100, 200, and 300 units. The lowest curve was measured on a loose, pre-bended, sample. This shows strong resonances above 1 kHz. The intermediate curves correspond to samples clamped taut under 0 and 13% strain. The resonances are hardly suppressed. However, backing the PVDF with polystyrene foam does suppress the resonances (upper curve) effectively.

Both the bending and (high frequency) tensile contribution can be reduced by applying a thick layer of epoxy, cf. Fig.6. The higher the extent of cure of the resin the lower the remaining high-frequency piezo-contribution. However, such a solid backing introduces unwanted heat losses, which result in a lower pyrocurrent at low frequencies.

The LMM-data of LiTaO_3 in Fig.7 demonstrate that LiTaO_3 is more suitable in model-systems than PVDF, because it is fully crystalline and is much stiffer. Accordingly, hardly any piezoelectric contribution can be noticed in Fig.7.

Fig.7 Pyroelectric spectra of $75\mu\text{m LiTaO}_3$, a) with a $20\mu\text{m}$ paint coating and b) without. For a) both the in-phase and out-phase currents are shown.

4. Conclusions and recommendations

LMM-experiments on polymer films may suffer from several experimental errors, in particular when the properties are nonuniform or the samples are asymmetric. However, most errors can be corrected, e.g. by applying a calibration or by carefully checking the validity of the electrical or thermal model.

Two mechanisms should be addressed particularly, piezoelectricity and dielectric dispersion. The first can be suppressed with a (thermally insulating) backing, by taking symmetric samples (e.g. bimorphs) or by illuminating on two sides. The dielectric dispersion should be measured separately. It can then be accounted for by using a generalization of eqn.1.

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