Piezoelectric Resonances in the Dielectric Spectrum of Polymer Films

Piezoelectric polymer films have played an important role in sensor and actuator applications ever since high piezoelectric coefficients were reported in suitably prepared polyvinylidene fluoride (PVDF) in 1969 [1]. Subsequently, the same effect was found in odd-numbered polymides, copolymers of vinylidene cyanide (VDCN) and aromatic and aliphatic polyureas. Even though these polymers exhibit piezoelectric coefficients that are at least one order of magnitude smaller than those found in inorganic materials, such as lead zirconate titanate (PZT), they are nevertheless attractive for transducer applications in an aqueous environment, since their acoustic impedance is comparable to that of water. In addition, they can be easily patterned to form complex shapes covering large areas. Moreover, piezoelectric coefficients of several hundred pC/N have recently been reported in cellular polypropylene [2] and in layer systems with porous polytetrafluoroethylene films [3,4]. Several techniques have been used to determine the piezoelectric $d_{33}$ and $d_{31}$ coefficients [5]. The direct piezoelectric effect (generation of an electrical signal upon a change in mechanical stress) can be measured in a quasi-static experiment [4]. Alternatively, the inverse piezoelectric effect can be measured by applying an electric field to the film and detecting the change in thickness by, e.g., optical interferometry [6] or acoustical techniques [7]. As a consequence of their thermodynamic definition [8], the piezoelectric coefficients of the direct and indirect effect must be equal.

Most of the above-mentioned methods are limited to frequencies between 0 and 100 kHz. In recent years, high-resolution dielectric spectroscopy has been successfully used to characterize piezoelectric polymers at much higher frequencies. Apart from the piezoelectric coefficient, this technique also yields the elastic moduli and electromechanical coupling coefficients. In its basic form, the admittance $Y(\omega)$ of a sample forming a thin parallel-plate capacitor is recorded as a function of frequency. Near the thickness-extension (TE) mode anti-resonance frequency, the complex capacitance $C(\omega) = Y(\omega)/i\omega = C'(\omega) - iC''(\omega)$ is given by [9,10].

Fig. 1. Thickness-extension resonance of a 110 µm PVDF-TrFE film (Piezotech SA) at 40 °C. The solid and dashed lines were obtained by fitting Eq. (1) to the experimental data.

Fig. 2. Dielectric loss $C''$ of a 110 µm PVDF-TrFE film (Piezotech SA) versus frequency and inverse temperature. The maxima correspond to the fundamental and the third harmonic of the thickness-extension mode.
$\tilde{C}(\omega) = \frac{\varepsilon^s \varepsilon_r A}{h} \frac{1}{1-k_{33}^2 \tan(\omega/4f_p)} - i\varepsilon_{\text{loss}} \frac{1}{(\omega/4f_p)} \tan(\omega/4f_p)$

(1)

where $\varepsilon^s$ is the relative permittivity of the sample under constant strain, $A$ and $h$ are the electroded sample area and thickness, respectively, $k_{33}$ is the complex electromechanical coupling factor, and $f_p$ is the complex anti-resonance frequency of the TE mode. For a free-standing film, $f_p$ is related to the complex elastic stiffness $c_{33}^{\text{el}}$ under constant electric displacement and the sample density $\rho$ via

$$f_p = \frac{1}{2h} \sqrt{\frac{c_{33}^{\text{el}}}{\rho}}, \quad (2)$$

and the electromechanical coupling factor $k_{33}$ is given by

$$k_{33}^2 = \frac{c_{33}^2}{e^2} \left(\varepsilon^s \varepsilon_0 \varepsilon_{33}^D\right), \quad (3)$$

where the piezoelectric stress coefficient $e$ is related to the piezoelectric strain coefficient $d$ via $e/d = c$ [11]. The $-i\varepsilon_{\text{loss}}$ term in Eq. (1) accommodates the inherent dielectric loss of the sample. From the experimental data, the sample parameters $k_{33}$ and $f_p$ are determined via a non-linear least squares fit. Other methods of analysis have been suggested [12], but appear to be more likely to generate artefacts. $c_{33}^{\text{el}}$ and $d_{33}$ can then be calculated with Eqs. (2) and (3), respectively.

To accommodate mechanical losses, $f_p$ and $k_{33}$ must be treated as complex quantities. Piezoelectric polymer films investigated via the dielectric resonance method include PVDF [13] and vinylidene-trifluoroethylene copolymers (P(VDF-TrFE)) [14]. Figure 1 shows the complex capacitance of a commercial 110 µm P(VDF-TrFE) sample (Piezotech SA). The spectrum was acquired with a Novocontrol Concept80 dielectric spectrometer. Unlike molecular relaxations, where the full width at half maximum (FWHM) is 1.14 decades, resonance peaks are much narrower, thus requiring a high frequency resolution. When the resonance spectrum is acquired over a wide range of frequencies, it may be necessary to include the contribution from dipole relaxation in the form of, e.g., a Havriliak-Negami term, leading to a frequency-dependent $\varepsilon^s$. By acquiring the dielectric spectrum at different temperatures, the temperature dependence of $e^D$, $k_{33}$ and $d_{33}$ can be measured.

Figure 2 shows the dielectric loss of the same film as mentioned in Fig. 1. The data were acquired as a function of frequency under nearly isothermal conditions ($\Delta T_{\text{max}}=0.25 \text{ K}$) in 10 K intervals. The softening of the sample at higher temperatures results in a decrease of the anti-resonance frequency. Analyzing the dielectric spectra potentially requires a large number of least squares fits (one for each temperature). This task is best performed using high-level scripting languages such as Matlab or Gnuplot.

A recent study of corona-charged cellular polypropylene (PP) films showed dynamic piezoelectric coefficients of 140 pC/N at 600 kHz [15]. The large piezoelectric effect is caused by charges trapped at the surfaces of flat internal voids with lateral dimensions of approximately 100 µm and vertical dimensions of several µm which act as oriented macroscopic dipoles. The dielectric spectrum in Fig. 3 reveals TE as well as length (LE) and width-extension (WE) resonances. Due to their lower elastic modulus in the $z$ direction, the thickness-extension resonance frequency of porous polymers is typically one order of magnitude lower than that of their non-porous counterparts.

A different boundary condition can be imposed on the piezoelectric resonator by gluing the film onto a glass substrate with a thin layer of epoxy. In this case, the factor 2 in the denominator of Eq. (2) must be replaced by 4, thus lowering the TE
One drawback of the cellular PP films is their limited thermal stability. Very recently, corona-charged Teflon® AF amorphous fluoropolymer sandwich films were shown to exhibit strong piezoelectricity with coefficients of up to 600 pC/N [16]. From Figures 4 and 5 it is evident that the samples show only a small decrease in $d_{33}$ up to 120 °C.

In summary, dielectric spectroscopy is a convenient tool to investigate not only the electrical, but also the mechanical and electromechanical properties of polymer films, and will continue to play an important part in the search for new transducer materials.

References

Axel Mellinger
Department of Physics,
University of Potsdam,
Am Neuen Palais 10,
14469 Potsdam, Germany
Mail: axm@rz.uni-potsdam.de
Friedrich Kremer

**How to Analyse the Conductivity Contribution in Dielectric Spectra?**

The conductivity contribution in dielectric spectra is often an unwelcome artefact caused by charged impurities in a sample. Usually, it has in the imaginary part $\varepsilon^\prime\prime$ of the complex dielectric function a frequency dependence which can be described by the formal ansatz

$$\varepsilon^\prime\prime(\omega) = \frac{\sigma_0}{\omega} \cdot a$$

(1)

In this notation $\varepsilon_0$ is the vacuum permittivity, $\omega$ the angular frequency. For pure electronic conductors $s = 1$ and $\sigma_0$ describes the direct current (DC) conductivity with $a = 1$. In this case no contribution to $\varepsilon^\prime\prime$ is observed. For hopping conduction \[1\] in disordered systems $s < 1$ and the conductivity contribution becomes complex (the constant $a$ has then the dimension $[a] = (Hz)^{1-s}$). What is the molecular origin for this response and how should it be analysed?

The motion of a hopping charge is accompanied by an electrical relaxation: An ionic or electronic (in case of a polaron) charge is surrounded by negative or positive counter charges. A hop of a charge carrier to a new site can lead to a successful charge transport only if the polarisation cloud follows. Otherwise the charge carriers will jump back with a high probability. This mutual movement of the charge carrier and the surrounding polarisation cloud requires an electrical relaxation time $\tau_e$. If the frequency of the outer electrical field is higher than $1/\tau_e$ its effect on the charge transport averages out. For lower frequencies than $1/\tau_e$ the relaxation of the polarisation cloud is in phase with the outer electrical field. For that case the field supports the propagation of the charges. Hence this electrical relaxation gives rise to a contribution in the complex dielectric function which increases with decreasing frequency. This is the essence of the Debye / Hückel / Falkenhagen theory \[2-4\]. It explains the experimental observation that for electrolytes the real part $\varepsilon^\prime$ increases with decreasing frequency. (Additionally one has to expect electrode polarisation effects in ionic conductors.)

The random free energy barrier model as developed by Dyre \[5\] assumes that conduction takes place by hopping of charge carriers in a randomly varying energy landscape. It provides a basis to analyse the charge transport in disordered systems. Within the Continuous–Time-Random Walk (CTRW) approximation \[6\] the following expression for the complex conductivity $\sigma^*(\omega)$ is obtained

$$\sigma^*(\omega) = \sigma_0 \left[ \frac{i \omega \tau_e}{\ln(1 + i \omega \tau_e)} \right]$$

(2)

where $\tau_e$ is the attempt frequency to overcome the largest barrier determining the DC-conductivity. Splitting into real and imaginary parts delivers:

$$\sigma^\prime(\omega) = \frac{\sigma_0 \omega \tau_e \arctan(\omega \tau_e)}{4 \ln^2(1 + \omega^2 \tau_e^2) + (\arctan \omega \tau_e)^2}$$

$$\sigma^\prime\prime(\omega) = \frac{\sigma_0 \omega \tau_e \ln(1 + \omega^2 \tau_e^2)}{2 \ln^2(1 + \omega^2 \tau_e^2) + 2(\arctan \omega \tau_e)^2}$$

As example \[7\] spectra of the zwitter-ionic poly(3-M-[o-methacrylogloxyalkyl]-N, N-dimethyl ammonio|propane sulfonate) doped with 100 mol % NaI are analysed. It shows that the above formulae describe well the measured complex conductivity (Fig. 1). For the real part $\sigma^\prime(\omega)$ on the low frequency side a plateau value is obtained which can be extrapolated to the DC-conductivity.
At a critical frequency $\omega_c = 2\pi \nu_c$, the dispersion of $\sigma'$ sets in. The later can be determined by smoothing the data and calculating numerically the maximum in $\frac{\partial^2 \sigma' / \partial \omega^2}{\omega^2}$. The imaginary part of the complex conductivity decreases with decreasing frequency. The increase at low frequencies indicates electrode polarization. Of course it does not make a difference if the data are displayed in another representation, e.g. in

$$\varepsilon^* = \frac{\sigma'}{j\omega \varepsilon_0} + 1$$

or in the electrical modulus $M^* = \frac{1}{j\omega \varepsilon_0}$ (Fig. 2 resp. Fig. 3). From the fits the DC-conductivity $\sigma_0$ and the electrical relaxation time $\tau_e$ is obtained. As shown in Fig. 4 the Barton/Nakajima/Namikawa (BNN) [8a-c] relationship $\frac{1}{\tau_e} \sim \sigma_0$ is well fulfilled. This proves that DC- and AC-conduction are based on the same mechanism of charge transport.

It is remarkable that the complex conductivity $\sigma^*$ is similar in its frequency- and temperature (including also charge carrier

![Fig.2. Complex dielectric function for the data presented in Fig.1. Lines are fits of Eq. (2) to the data. For low frequencies the contribution due to electrode polarization (dashed line) is added.](image)

![Fig.4. Proof of the BNN-relationship: - data for the zwitter-ionic system (shown in Fig. 1-3) The line is a linear regression to these data. The inset compares relaxation times (or rates) for conduction estimated with different methods. $\sigma_0$ is the relaxation rate at the maximum in $M^*$ (see Fig. 3).](image)
concentration)-dependence for a broad variety of quite different materials, e.g. ionic glasses, ion conducting polymers, electron conducting conjugated polymers or electron conducting carbon black composites.

References

Friedrich Kremer
University of Leipzig,
Department of Physics,
Linnéstrasse 5,
04103 Leipzig, Germany
Mail: kremer@physik.uni-leipzig.de

Fig. 3. Complex electric modulus for the data presented in Fig. 1. Lines are due to fits of Eq. (2) to the data.
OVERVIEW
BROADBAND DIELECTRIC SPECTROSCOPY
over 16 decades by NOVOCONTROL

Factory and Head Office

Germany:
NOVOCONTROL GmbH
Obererbacher Straße 9
D-56414 Hundsangen / GERMANY
Phone: ++(0) 64 35 - 96 23-0
Fax: ++(0) 64 35 - 96 23-33
Mail novo@novocontrol.com
Web http://www.novocontrol.com

Agents

Benelux countries:
NOVOCONTROL Benelux B.V.
Postbus 231
NL-5500 AE Veldhoven / NETHERLANDS
Phone ++(0) 40 - 2894407
Fax ++(0) 40 – 2859209

South-East Asia:
ITS Science & Medical Pte. Ltd.
219 Henderson Road #011-02
Singapore 159 556
Phone ++(0) 65 2730-898
Fax ++(0) 65 2730-810
Mail its-sm@its-asia.com
Contact: Mr. Tony Lee

USA/Canada:
NOVOCONTROL America Inc.
611 November Lane / Autumn Woods
Willow Springs, North Carolina 27592-7738 / USA
Phone: ++(0) 919 639 9323  Toll free  1-877-639-9323
Fax: ++(0) 919 639 7523
Mail novocontrolusa@earthlink.net
Contact: Mr. Joachim Vinson, PhD

Korea:
PST Polymer Science & Technology
P.O Box 122, Budang
Sungnam-Shi, Kyounggi-Do, Korea or
Rm. 2103, Woosung Character 199,
467-24 Dogok-Dong, Kangnam-Gu, Seoul, Korea
Phone ++ 82-502 710 7100
Fax: ++ 82 502 710 7200
Mail seapoint@hananet.net
Contact: Mr. Young Hong

Japan:
Morimura Bros. Inc.
2 nd chemical division
Morimura Bldg. 3-1, Toranomon 1-chome
Minato-Ku
Tokyo 105 / Japan
Phone: ++(0) 3-3502-6440
Fax: ++(0) 3-3502-6437
Mail hasegawa@morimura.co.jp
Contact: Mr. Hasegawa

People's Rep. Of China:
GermanTech
Jing Min Building Room 2915
Hua Yan Li No. 10, Chaoyang District
100029 Beijing
Phone: ++(10) 8207393
Fax: ++(10) 8207995
Mail germttech@public3.bta.net.cn
Contact: Xintao Li, PhD

Taiwan (R. O. C.) :
Advantage Scientific Inc.
P.O. Box 44-238
Taipei
Phone ++(02) 2733-2422
Fax: ++(02) 2737-5575
Mail alie4net@ms8.hinet.net
Contact: Mr. Paolo Cheng
Information request

Company / Institute ......................................................................................................................
Name ........................................................................................................................................
Street ....................................................................................................................................... 
City .......................................................................................................................................... 
Postal Code .............................................................................................................................. 
Country ..................................................................................................................................... 
Phone ....................................................................................................................................... 
Fax ............................................................................................................................................ 
Email .........................................................................................................................................

Broadband Dielectric Spectrometers

☑ Economical dielectric spectrometers (3 μHz - 300 kHz or 3 μHz - 3 MHz)
☑ Top class dielectric spectrometer (3 μHz - 10 MHz)
☑ GHz dielectric spectrometer (1 MHz – 1.8 / 3 / 8 GHz)

New Instruments and Modules

☑ TSDC instruments and WinTSC software
☑ Pressure dependent dielectric spectrometers (0 - 3000 bar)
☑ ALPHA high resolution dielectric analyzer (3 μHz - 10 MHz)
☑ ALPHA high voltage extension (+150Vp ac and / or dc, 3 μHz – 1 MHz)
☑ Spin coaters

Software

☑ MS-Windows software for automatic measurement of dielectric relaxations, impedance, electrical and magnetic material properties
☑ MS-Windows software for automatic curve fitting data analysis (WLF, VF) and equivalent circuit transformation

Application Notes, Dielectrics Newsletters

Please visit our web page http://www.novocontrol.com for free downloads

Optional temperature control systems

☑ Novotherm +20°C .. +400°C
☑ Novocool -100°C .. +250°C
☑ Quatro -160°C to +500°C

Status of my request

☑ Urgent demand. Please send me also a quotation.
☑ Future demand
☑ General interest