Polymer Testing 37 (2014) 163–169

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Test method

Electromechanical characterization of piezoelectric polymer thin films in a broad frequency range

M.G. Gonzalez [a], [b], [*], P.A. Sorichetti [c], L. Ciocci Brazzano [a], [b], G.D. Santiago [a]

[a] *Grupo de Láser, Óptica de Materiales y Aplicaciones Electromagnéticas (GLOMAE), Departamento de Física, Facultad de Ingeniería, Universidad de Buenos Aires, Paseo Colón 850, C1063ACV, Buenos Aires, Argentina*
[b] *Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina*
[c] *Grupo de Sistemas Dispersos-Laboratorio de Sistemas Líquidos (GSD-LSL), Departamento de Física, Facultad de Ingeniería, Universidad de Buenos Aires, Paseo Colón 850, C1063ACV, Buenos Aires, Argentina*

ARTICLE INFO

Article history:
Received 22 April 2014
Accepted 28 May 2014
Available online 10 June 2014

Keywords:
Piezoelectric thin films
Broadband electromechanical characterization
Ultrasonic transducers
Medical imaging
Clamped piezoelectric
Poly(vinylidene fluoride) – PVDF
Permittivity
Elastic compliance

ABSTRACT

Piezoelectric materials are usually characterized using resonant methods. However, piezoelectric polymers are used in broadband devices, thus requiring characterization over a wide range of frequencies. In this work, we present a non-resonant method for the broadband electromechanical characterization of piezoelectric polymer thin films. The procedure is based on measuring the complex capacitance of a sample of known geometry under three conditions: free, blocked and immersed in a fluid of known acoustic properties. The behaviour of the sample under study is modelled as a one-dimensional transducer and treated as a two-port network that relates the measurable electrical and mechanical variables. Also, the sample is considered as a free-space radiator when immersed in a fluid. The method determines the intensive and the equivalent circuit parameters of piezoelectric polymer films, allowing the characterization of elastic and electrical properties in a broad frequency range.

In order to test the method, we performed isothermal capacitance measurements on a sample of poly(vinylidene fluoride) at a temperature of 298 K. The sample was measured along the direction of the poling field and in the frequency range from 10 Hz to 10 MHz. The results given by the method agree with those reported by other authors.

1. Introduction

The electromechanical characterization of piezoelectric materials is usually carried out by measuring the electrical impedance of the sample at a mechanical resonance [1–9]. This gives good results when applied to low-loss materials used in narrowband transducers. However, characterization methods based on resonance have limited applicability for measurements over a wide range of frequencies, and also for material with higher losses. This paper presents a non-resonant method to characterize piezoelectric polymer films in a broad frequency range. The procedure is tested by determining the intensive parameters of poly(vinylidene fluoride) (PVDF) piezoelectric film in the frequency range from 10 Hz to 10 MHz.

2. Method

The thin film polymer sample is modelled as a one-dimensional (1D) transducer. Therefore, it can be treated as a two-port network that relates electrical quantities at one port to mechanical quantities at the other, as shown in Fig. 1 [10]. The measured electrical quantities are the

---

[*] Corresponding author. Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina.

E-mail addresses: mggonza@fi.uba.ar, mggonza@gmail.com (M.G. Gonzalez).

http://dx.doi.org/10.1016/j.polymertesting.2014.05.014

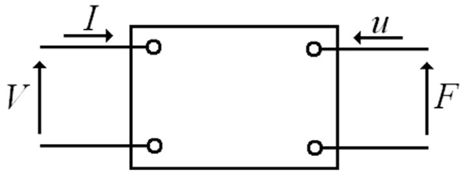

Fig. 1. Two-port network where force is the analog of voltage and speed is the analog of current.

voltage across the sample (V) and the current through the sample (I). The mechanical quantities are the force (F) and the velocity (u) integrated over the surface of the sample. In this work, the force is considered as the analog of voltage, and the speed the analog of current. The four measurable admittances associated with the extensive electrical and mechanical variables of the system are: 1) the electrical admittance at zero strain condition (blocked) $Y_{EB} = I/V|_{u=0}$, 2) the electrical admittance at zero stress condition (free) $Y_{EF} = I/V|_{F=0}$, 3) the mechanical admittance at open-circuit condition $Y_{mo} = u/F|_{I=0}$, and 4) the short-circuit mechanical admittance $Y_{ms} = u/F|_{V=0}$. Uppercase subscripts designate electrical parameters, lowercase subscripts mechanical ones, and the second subscript refers to the measurement condition.

In the 1D approximation, the electromechanical behaviour of the sample is described by two equations:

$$I = Y_{EF} \cdot V + T \cdot F \tag{1}$$

$$u = T \cdot V + Y_{ms} \cdot F \tag{2}$$

where T is a transduction coefficient.

In this method, the sample is considered as a free-space radiator. It follows that, when the sample is immersed in a fluid and acts as a source, the integrated force and velocity are related by $u = -Y_r \cdot F$ where Y_r is the radiation admittance, which depends on the fluid properties and the geometry of the sample. The two limiting cases correspond to the free sample, when $|Y_r| \to \infty$, and the blocked condition, when $|Y_r| \to 0$.

During manufacture, the piezoelectric polymer film, such as PVDF, is stretched and then poled by applying an electric field in the direction perpendicular to the film. As usual, the stretching direction (in the plane of the film) is indicated as the reference axis 1 and the poling direction is indicated as the reference axis 3. In this work, all the properties were measured in the direction of the poling field.

From the constitutive equations applied to a 1D thin piezoelectric film, it is possible to relate the extensive parameters of (1) and (2) and the intensive parameters which characterize the sample. Under harmonic excitation of frequency f it results in:

$$T = j \cdot 2 \cdot \pi \cdot f \cdot d_{33}(f) \tag{3}$$

$$Y_{ms} = j \cdot 2 \cdot \pi \cdot f \cdot \delta / A \cdot s_{33}(f) \tag{4}$$

$$Y_{EF} = j \cdot 2 \cdot \pi \cdot f \cdot A / \delta \cdot \varepsilon_{33}^{F}(f) \tag{5}$$

where d_{33} is the piezoelectric coefficient, s_{33} the elastic compliance at constant electric field, ε_{33}^{F} the complex permittivity at zero stress condition and δ y A the thickness and the area of the film, respectively.

The method is based on measuring the complex capacitance of a sample of known geometry under three conditions: a) free, b) blocked, c) immersed in a fluid whose density and speed of sound are known. As an alternative, the blocked-condition test can be replaced with the sample immersed in a fluid with an acoustic impedance much larger than the short circuit mechanical impedance of the sample (and therefore $|Y_r| << |Y_{ms}|$). The complex capacitances are related to the measured electric admittances as follows:

$$Y_{EF} = j \cdot 2 \cdot \pi \cdot f \cdot C_{EF}(f) \tag{6}$$

$$Y_{EI} = j \cdot 2 \cdot \pi \cdot f \cdot C_{EI}(f) \tag{7}$$

$$Y_{EB} = j \cdot 2 \cdot \pi \cdot f \cdot C_{EB}(f) \tag{8}$$

The free and blocked intensive parameters are related by [11]:

$$\varepsilon_{33}^{F} = \varepsilon_{33}^{B} + d_{33}^{2} \Big/ s_{33} \tag{9}$$

In addition, when the sample acts as a free-space radiator, (9) must be extended to include the radiation impedance. From (1) and (2), for the immersed condition results in:

$$Y_{EI} = Y_{EF} - \frac{T^2}{Y_{ms} + Y_r} \tag{10}$$

This, in terms of the intensive parameters, can be given as:

$$\varepsilon_{33}^{I} = \varepsilon_{33}^{F} - d_{33}^{2} \Big/ [s_{33} + s_r] \tag{11}$$

where s_r is the equivalent compliance, related to the radiation admittance by:

$$s_r = -j \cdot \frac{A}{\delta} \cdot \frac{Y_r}{2 \cdot \pi \cdot f} \tag{12}$$

Using (9) and (11), the intensive parameters d_{33} and s_{33} could be computed. However, this is not a convenient choice because that pair of equations is numerically “ill-conditioned”.

In this work, we assume that the polarization instantaneously follows the mechanical deformation. This can be justified by noting that the total piezoelectric effect due to deformation can be written as a sum of two terms of different origins: i) volume change and ii) reorientation of the elementary dipoles of the crystalline phase. Although we cannot exclude *a priori* the existence of a delay between deformation and dipole reorientation in the crystalline phase, according to the work of Broadhurst et al. [12] the effect of volume change is clearly predominant in PVDF, as is the case in most piezoelectric polymers. Hence, there is no serious error if the reorientation delay is neglected. Therefore, from (9) it follows that the difference between the free and blocked permitivities is proportional to the elastic compliance, i.e. d_{33} is proportional to s_{33}:

$$d_{33} = \sigma_{33} \cdot s_{33} \tag{13}$$

where σ_{33} is the equivalent surface charge density of remnant polarization and under this assumption is a real number, within the relevant frequency range.

Given an initial value of σ_{33}, the s_{33} spectrum is obtained using (9). Then, σ_{33} and s_{33} are used to evaluate the complex permittivity at the immersed condition using (11). This spectrum is compared with the measured one and iterations are repeated until the calculated spectrum converges to within a given tolerance.

3. Measuring setup and materials

A PVDF sample (PIEZOTECH CORP) with a thickness of 25 μm, metalized on both sides, was cut as a disk 6 mm in diameter.

The sample in the clamped condition was placed between two thick metallic disk electrodes tightly held together. In the other measurements, electrical connections to the sample were made with two short (5 mm) copper wires of small diameter (100 μm), bonded to the periphery of the metalized surfaces of the sample with speckles of conductive silver paint. Regarding the accuracy of the measurements, it is important to ensure good electrical connections while minimizing the mechanical loading of the sample.

For measurements in the immersed condition, sunflower oil was used because its acoustic properties are similar to water (its density and speed of sound values at 25 °C are 919 kg/m^3 and 1454 m/s respectively), it is chemically compatible with PVDF and does not alter the electrical connections to the sample. Moreover, sunflower oil is readily available, has negligible electrical conductivity and low permittivity [13] compared to water. Silicone oil (Dow Corning 704) was also considered for immersed measurements. It is chemically compatible with PVDF and its electrical and acoustic properties are adequate. However, it could not be used in this work since extensive tests showed that the bonds of the connection wires to the sample degraded quickly when immersed in silicone oil, resulting in unreliable experimental results.

The sample was placed in a glass enclosure, in a Lauda thermostatic bath stabilized at 298 K ± 0.02 K. The temperature was measured within ±0.1 K with a calibrated thermocouple placed next to the sample. The temperature in the laboratory was stabilized at 299 K ± 1 K. In the case of free and blocked conditions, the glass enclosure was also flushed with dry nitrogen. The size of the glass container must be large enough to ensure the immersed sample behaves as a free-space radiator (the reflections in the walls may be neglected). It must be noted that, for piezoelectric polymers such as PVDF, measurements with the sample in air may be considered as free ($|Y_r| << |Y_{ms}|$).

The samples in the thermostat were connected to the dielectric measuring interface with a very short length (10 cm) of low-loss coaxial cable (with a nominal impedance of 50 Ω). The impedance and propagation delay of the cable were accurately determined with an automated reflection bridge at frequencies up to 30 MHz. We emphasize that the accurate characterization of the cable is essential to correct the systematic errors in measurements at high frequencies, where the cable length is not negligible in comparison to the signal wavelength.

The dielectric measuring interface, together with the measurement method and the calibration procedures were described in detail in a previous work [14]. Two different

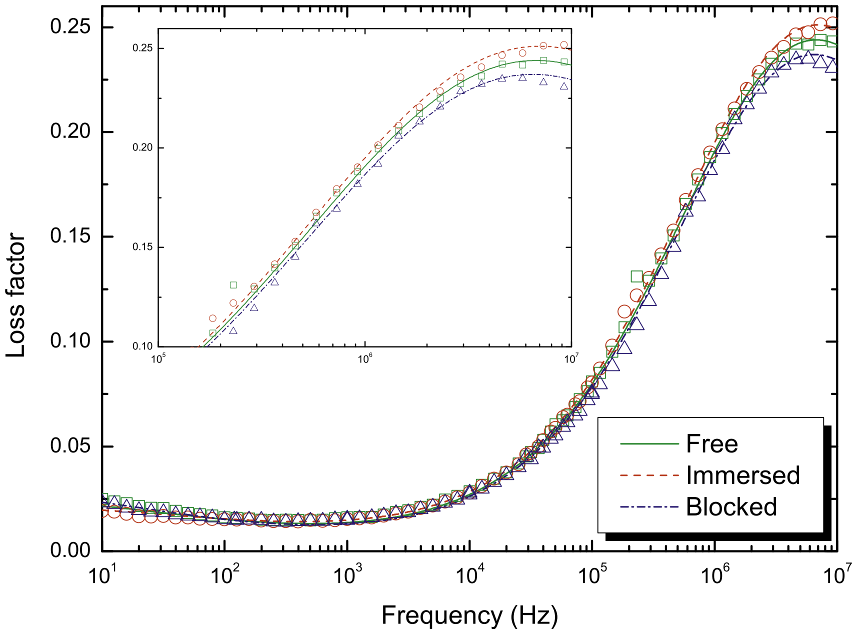

Fig. 2. Loss factor in the three conditions: free (solid line and squares), immersed (dashed line and circles) and blocked (dashdot line and triangles). Symbol: experimental data. Solid line: HN function with the fitting parameters from Table 1.

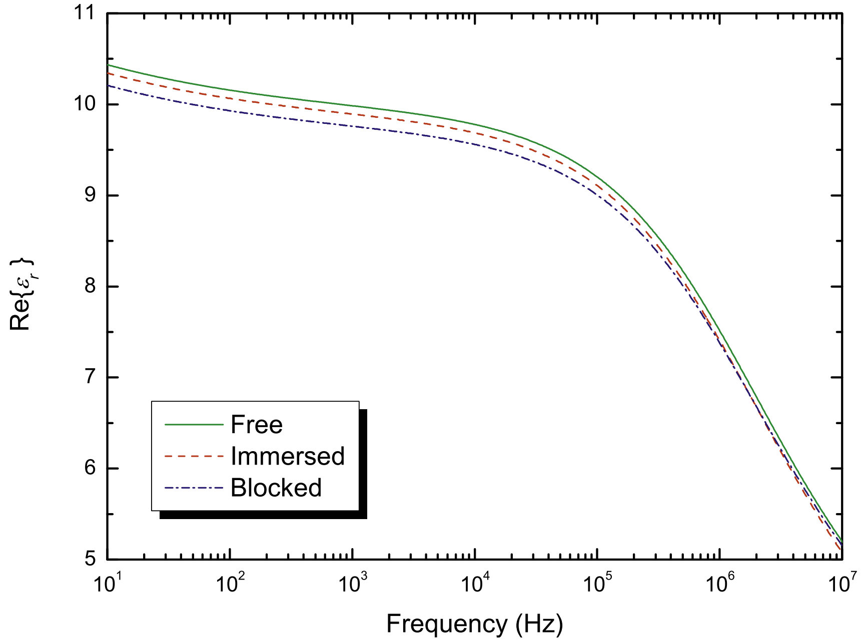

Fig. 3. Real part of the complex permittivity for the sample in conditions: free (solid line), immersed (dashed line) and blocked (dashdot line).

setups were employed for magnitude and phase measurements of the signals from the measuring interface. At low frequencies, between 10 Hz and 100 kHz, a Stanford Research SR-810 Lock-in Amplifier was used, and its internal source provided the excitation signal. In the frequency range from 20 kHz to 10 MHz, the excitation was provided by an Instek GW-830 synthesized signal generator, captured with a Tektronix TDS 210 real-time, digital-sampling oscilloscope, and processed with an FFT routine. We checked the overlap of experimental results from both sets of instruments in the frequency range between 20 kHz and 100 kHz. As an additional verification, we made measurements at 1 kHz, 10 kHz and 100 kHz using a stand-alone RCL Meter (Tonghui 2822C).

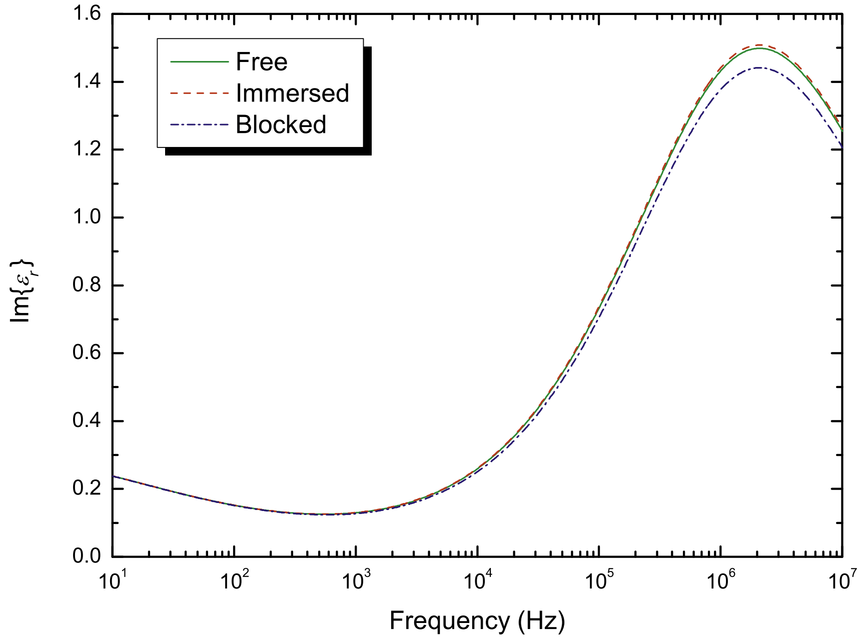

Fig. 4. Imaginary part of the complex permittivity for the sample in conditions: free (solid line), immersed (dashed line) and blocked (dashdot line).

Table 1
Fitted parameters of Havriliak-Negami function for the sample in the three conditions.

	C_∞ (pF)	ΔC_H (pF)	α_H	β_H	τ_H (ns)	ΔC_L (pF)	α_L	β_L	τ_L (s)
Free	31.5	78	0.5	0.68	140	17	0.46	0.68	0.2
Immersed	30	78.5	0.5	0.68	140	17	0.4	0.68	0.2
Blocked	32	75	0.5	0.68	140	17	0.5	0.68	0.2

3. Results

In thin film, the free and blocked capacitances result in

$$C_{EB,F} = \varepsilon_{B,F} \cdot A/\delta \tag{14}$$

In Ciocci Brazzano et al. [15] we show that the permittivity of the PVDF can be described by a Havriliak-Negami (HN) function [16]. Therefore, the measured capacitance can be described by,

$$C_E = C_\infty + \Delta C_H/[1 + (j\cdot\omega\cdot\tau_H)^{\alpha_H}]^{\beta_H} + \Delta C_L/[1 + (j\cdot\omega\cdot\tau_L)^{\alpha_L}]^{\beta_L} \tag{15}$$

where C_∞ is the limiting value of the capacitance at high frequencies, ΔC the relaxation strength, τ the characteristic relaxation time, and α and β are shape parameters that describe the broadening of the relaxation peak; the subscripts H and L denote relaxation peak at high and low frequencies, respectively. The parameters of (15) depend on the measurement conditions. In the immersed condition, the measured capacitance includes the effects of the radiation admittance, as can be seen from (10).

Fig. 2 shows the measurements of the loss factor and the corresponding fittings using (15). Figs. 3 and 4 depict the dielectric spectra (real and imaginary, respectively) at the three conditions given by the parameters of Table 1. In all cases, the root-mean-square error (RMSE) in the fitting is less than 0.3 pF. Comparing these results with those reported in a previous work [15], it is interesting to note that the peak in the imaginary part between 1 kHz and 10 kHz, which is shown in Fig. 2 of [15], is absent in the spectra presented in this work. After a thorough check of our data, we conclude that poor connections between the metalized surface of the sample and the connection wires were responsible for this artifact. This emphasizes the need to carefully select the fluid used for the measurements in the immersed condition in order to ensure good electrical connections to the sample.

From these measurements, it is possible to compute the electromechanical coupling coefficient, a parameter widely used to describe resonant transducers [11]. According to our data, the PVDF sample has an electromechanical coupling of 0.15 (almost constant and with a negligible imaginary part within the studied frequency range), a result within the range of previous reports carried out by resonant methods (0.07-0.2) [5].

To calculate the radiation admittance, Y_r, the immersed sample is considered as a resilient disk in free space. According to the result of Mellow [17]:

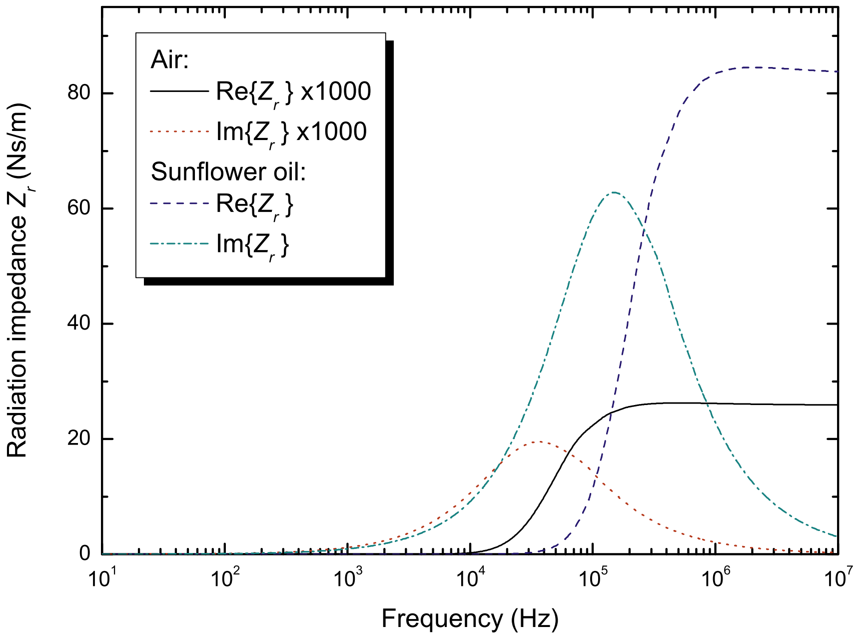

Fig. 5. Radiation Impedance for air (free condition) and sunflower oil (immersed condition).

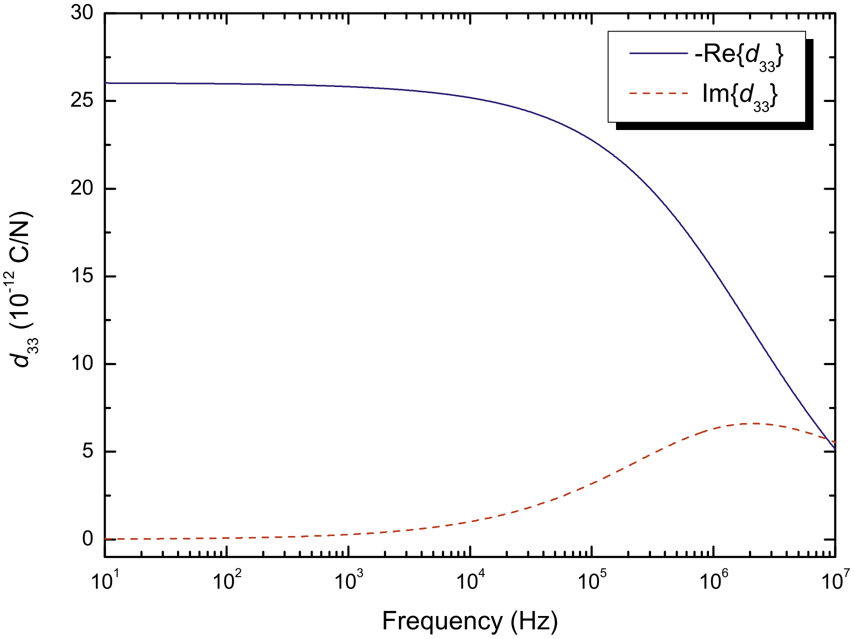

Fig. 6. Complex piezoelectric coefficient of the sample.

$$Y_r = \frac{1}{2\cdot\rho_L\cdot c_L\cdot\pi\cdot a^2}\bullet[G_{rn}(k\cdot a) - j\cdot B_{rn}(k\cdot a)] \tag{16}$$

The normalized radiation conductance, G_{rn}, and susceptance, B_{rn}, are given by:

$$G_{rn} = 1 + \frac{J_1(2\cdot k\cdot a)}{k\cdot a} - 2\bullet J_0(2\cdot k\cdot a) - \pi\cdot[J_1(2\cdot k\cdot a)\cdot H_0(2\cdot k\cdot a) - J_0(2\cdot k\cdot a)\cdot H_1(2\cdot k\cdot a)] \tag{17}$$

$$B_{rn} = \frac{4}{\pi\cdot k\cdot a} - \frac{H_1(2\cdot k\cdot a)}{k\cdot a} + \frac{4\cdot k\cdot a}{\pi}\cdot {}_2F_3\left(1, 1; \frac{3}{2}, \frac{3}{2}, 2; -k^2\cdot a^2\right) \tag{18}$$

where a is the radius of the disk, ρ_L and c_L the density and sound velocity of the medium, k the wave number, J_n the Bessel function of the first kind, H_n the Struve function and ${}_pF_q$ the hypergeometric function. Fig. 5 shows the real and imaginary part of the radiation impedance, $1/Y_r$, in air (free) and immersed conditions. It can be seen that PVDF in oil is an efficient radiator above 2 MHz, with a consequent increase

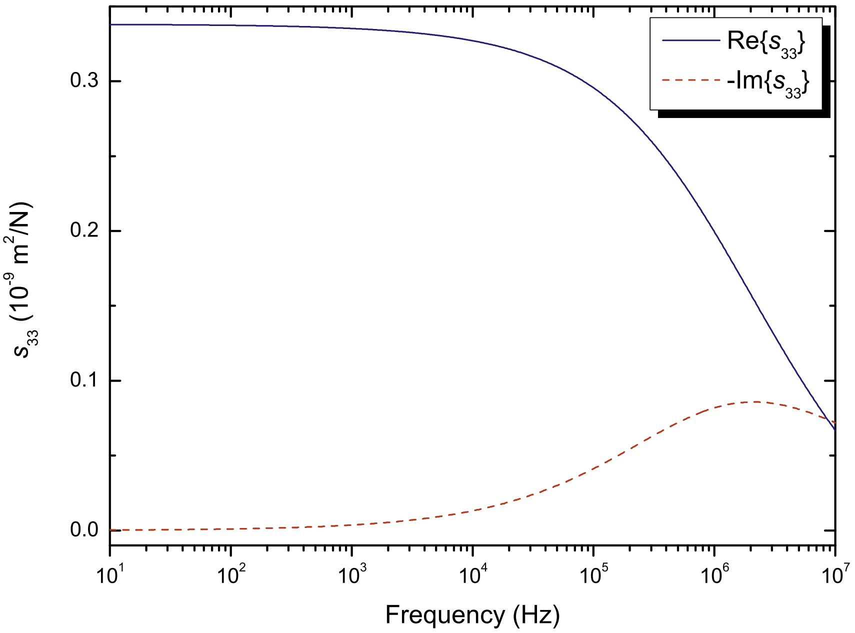

Fig. 7. Complex elastic compliance of the sample at constant electric field.

of the loss factor compared to the sample at free condition (see Fig. 2). Moreover, the large magnitude difference between the two conditions is evident from the figure.

To accelerate the convergence of the iterative procedure, the initial estimation of s_{33} was the low-frequency value given by Thompson [18] (since in the low frequency limit, $|Y_r| \to \infty$). The low-frequency value of d_{33} was taken as 18 pC/N from the manufacturer's data.

The value of σ_{33} that best fits the immersed measurements is 7.7 μC/cm^2, which is consistent with the sample used in this work [1,12,19]. For this value, RMSE between the measured spectra and the final iteration was less than 0.3 pF for both the real and imaginary parts.

The plots in Figs. 6 and 7 show the frequency dependence of d_{33} and s_{33}. (Fig. 7) clearly reveals a process of elastic relaxation in the MHz range, typical of a polymer. On the other hand, the behaviour of d_{33} can be explained by the model given by Mocellini et al. [20]. At high frequencies the sample is stiffer since the elastic compliance decreases. This implies a reduction of the strain at constant force and, as a consequence, a decrease of the piezoelectric effect. Similar behaviour of d_{33} has been found in PVDF copolymers [21].

The values of d_{33} and s_{33} at frequencies near the first mechanical resonance lie within the range found in other works based on resonance methods [1,5–9].

4. Conclusions

In this work we present a method for broadband electromechanical characterization of piezoelectric polymer thin films. The method is based on measuring the complex capacitance of a sample of known geometry under three conditions: free, blocked, and immersed in a fluid of known acoustic properties. The sample under study is modelled as a one-dimensional transducer and treated as a two-port network that relates electrical and mechanical variables, considering the immersed sample as a free-space radiator.

In order to validate the method, we performed broadband isothermal capacitance measurements on a sample of PVDF at a temperature of 298 K. The sample was measured along the direction of the poling field and in the frequency range from 10 Hz to 10 MHz. The results given by the method are consistent with those reported by other authors at different frequencies.

It is interesting to note that, if the elastic compliance s_{33} at low frequency (where $|Y_r| \to \infty$) is known, capacitance measurements in the free and blocked conditions suffice to calculate all the intensive parameters, in the full measured frequency range.

In summary, the method presented in this work gives the permittivity and elastic compliance spectra at frequencies far below the first mechanical resonance. This is quite relevant for the characterization of piezoelectric polymer thin films and for the design and characterization of broadband ultrasonic transducers, such as hydrophones and medical imaging systems.

Acknowledgements

This work was supported by the University of Buenos Aires, grants UBACYT-20020100300035, UBACYT-20020090100136 and UBACYT-20020100100406; Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), grant PIP-112-201101-00676; and the Agencia Nacional de Promoción Científica y Tecnológica, grant PICT-2011-01211. Also, a post-doctoral grant from CONICET for one of the authors is gratefully acknowledged.

References

[1] H. Ohigashi, Electromechanical properties of polarized polyvinylidene fluoride films as studied by the piezoelectric resonance method, J. Appl. Phys. 47 (1976) 949.
[2] R. Lerch, Electroacoustic properties of piezopolymer microphones, J. Acoust. Soc. Am. 69 (1981) 1809.
[3] D.R. Bacon, Characteristics of a PVDF membrane hydrophone for use in the range 1-100 MHz, IEEE Trans. Sonics Ultrason. SU-29 (1982) 18.
[4] H.J. Bleeker, P.A. Lewin, A novel method for determining calibration and behaviour of PVDF ultrasonic hydrophone probes in the frequency range up to 100 MHz, IEEE Trans. Ultrason. Ferroelectr. Freq. Contr. 47 (2000) 1354.
[5] K.W. Kwok, H.L. Wah Chan, C.L. Choy, Evaluation of the material parameters of piezoelectric materials by various methods, IEEE Trans. Ultrason. Ferroelect. Freq. Contr. 44 (1997) 733.
[6] R.S. Dahiya, M. Valle, L. Lorenzelli, SPICE model for lossy piezoelectric polymers, IEEE Trans. Ultrason. Ferroelect. Freq. Contr. 56 (2009) 387.
[7] IEEE Std. 176-1978, IEEE Standard on Piezoelectricity, The Institute of Electrical and Electronics Engineers, New York, 1978.
[8] J.G. Smits, Iterative method for accurate determination of the real and imaginary parts of the materials coefficients of piezoelectric ceramics, IEEE Trans. Sonics Ultrason. SU-23 (1976) 393.
[9] S. Sherrit, H.D. Wiederick, B.K. Mukherjee, Non-iterative evaluation of the real and imaginary material constants of piezoelectric resonators, Ferroelectrics 134 (1992) 111.
[10] L.E. Kinsler, A.R. Frey, A.B. Coppens, J.V. Sanders, Fundamentals of Acoustics, John Wiley & Sons, New York, 2000.
[11] K. Uchino, Loss mechanisms in piezoelectrics: how to measure different losses separately, IEEE Trans. Ultrason. Ferroelectr. Freq. Contr. 48 (2001) 307.
[12] M.G. Broadhurst, G.T. Davis, J.E. McKinney, R.E. Collins, Piezoelectricity and pyroelectricity in polyvinylidene fluoride—a model, J. Appl. Phys. 49 (1978) 4992.
[13] J. Corach, P.A. Sorichetti, S.D. Romano, Electrical properties of vegetables oils between 20 Hz and 2 MHz, Int. J. Hydrogen Energy 39 (2014) 8754.
[14] P.A. Sorichetti, C.L. Matteo, Low-frequency dielectric measurements of complex fluids using high-frequency coaxial sample cells, Measurement 40 (2007) 437.
[15] L. Ciocci Brazzano, P.A. Sorichetti, G.D. Santiago, M.G. González, Broadband dielectric characterization of piezoelectric poly(vinylidene fluoride) thin films between 278 K and 308 K, Polym. Test. 32 (2013) 1186.
[16] S. Havriliak, S. Negami, A complex plane analysis of α-dispersions in some polymer systems, J. Polym. Sci. Polym. Sym. 14 (1966) 99.
[17] T. Mellow, On the sound field of a resilient disk in free space, J. Acoust. Soc. Am 123 (2008) 1880.
[18] M.L. Thompson, On the Material Properties and Constitutive Equations of Piezoelectric Poly Vinylidene Fluoride (PVDF), Ph.D. dissertation, Drexel University, Philadelphia, Pennsylvania, USA, 2002.
[19] F. Bauer, PVDF shock sensors: applications to polar materials and high explosives, IEEE Trans. Ultrason. Ferroelect. Freq. Contr. 47 (2000) 1448.
[20] R.R. Mocellini, G.I. Zelada-Lambri, O.A. Lambri, C.L. Matteo, P.A. Sorichetti, Electrorheological description of liquid and solid dielectrics applied to two-phase polymers: a study of EPDM, IEEE Trans. Dielectr. Electr. Insul. 13 (2006) 1358.
[21] A.V. Bune, C. Zho, S. Ducharme, L.M. Blinov, V.M. Fridkin, S.P. Palto, N.G. Petukhova, S.G. Yudin, Piezoelectric and pyroelectric properties of ferroelectric Langmuir–Blodgett polymer films, J. Appl. Phys. 85 (1999) 7869.