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**Wide-band electrical and electromechanical properties of polyvinylidene fluoride (PVDF) and polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE) piezoelectric films using Electro-Acoustic Reflectometry**

É. Maréchal, E. Géron, and S. Holé

*Laboratoire de Physique et d'Étude des Matériaux (UMR8213),*

*CNRS – ESPCI Paris, PSL University – Sorbonne University, 10 rue Vauquelin,*

*Paris, 75005, France<sup>a</sup>*

(Dated: 1 April 2023)

1 Thin piezoelectric polymer films are used in more and more high frequency applica-  
2 tions. However they are not well characterized up to the gigahertz range. In this  
3 paper, polyvinylidene fluoride (PVDF) and polyvinylidene fluoride-trifluoroethylene  
4 (PVDF-TrFE) films are mechanically and electrically characterized using the Electro-  
5 Acoustic Reflectometry (EAR) method from 20 MHz to 2 GHz. In addition to me-  
6 chanical and electrical properties, nonuniform poling is detected in the tested PVDF-  
7 TrFE samples showing a larger piezoelectric constant in the middle of the film and  
8 thus generating both even and odd resonance modes.

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<sup>a</sup>[stephane.hole@espci.fr](mailto:stephane.hole@espci.fr)

9      Keywords: Piezoelectric polymer films; dielectric properties; electromechanical proper-  
10 ties; Electro-Acoustic Reflectometry (EAR).

## 11 I. INTRODUCTION

12 Piezoelectric materials have found applications in numerous areas. Since their discovery<sup>1</sup>  
13 polarized polyvinylidene fluoride (PVDF) polymer films have shown good piezoelectric prop-  
14 erties that can provide an alternative to piezoelectric crystals: polymers are indeed flexible,  
15 can be made very thin, are soft, have a low thermal conductivity, and are generally low  
16 cost. In addition, they can be easily patterned to form complex shapes covering large ar-  
17 eas. Their softness makes them particularly well suited to be coupled with fluids since their  
18 acoustic impedance is comparable to that of water. They have found many applications in  
19 sensors and photonics, and their use is compatible with microelectronics<sup>2-5</sup>. Piezoelectric  
20 films in the micrometer thickness range correspond to higher frequency applications (up to  
21 the gigahertz range), that are now reachable at moderate cost with the progress of high fre-  
22 quency electronic devices. The characterization of the full properties (electrical, mechanical,  
23 uniformity) of these piezoelectric films, particularly at very high frequency, is therefore of  
24 interest.

25 When synthesized, PVDF polymer films are not polarized (nor piezoelectric): permanent  
26 polarization and piezoelectricity is achieved with different methods that consist in aligning  
27 the polar molecules in the same direction<sup>1</sup>. The standard method to permanently polarize  
28 the films, known as poling method, consists in applying a static electric field as high as  
29 about 300 kV/mm along the film thickness when the polymer is heated to about 100°C.  
30 Before poling, the films generally have been initially stretched to several times of their  
31 initial size at a slightly higher temperature, up to 150°C. After poling, a slow cooling down

32 to room temperature in the presence of the electric field prepares the film with a uniform  
33 dipole distribution through the film thickness responsible for piezoelectricity. For rather  
34 thick films (larger than  $100 \mu\text{m}$ ), the growing of the poling process was studied using the  
35 Pressure-Wave-Propagation Method (PWP)<sup>6</sup>. So far, it has not been tested for thinner  
36 samples owing to the lack of appropriate measurement method.

37 Recently, a measurement method called the Electro-Acoustic Reflectometry (EAR) has  
38 been proposed to break the limit of spatial resolution and reach the sub-micrometer range  
39 for the space charge distributions in dielectric films<sup>7</sup>. The EAR method is based on the  
40 measurement of the electro-elastic coupling in the material due to an electrical excitation  
41 swept over a very large frequency range. The electro-elastic coupling at each excitation fre-  
42 quency is extracted from the electrical impedance of the sample. Finally, from the variation  
43 of the electro-elastic coupling as a function of frequency, the charge distribution is recovered  
44 by an inverse Fourier transform. This method is particularly relevant for the characteriza-  
45 tion of thin piezoelectric films since the signal is proportional to  $\partial e_{33}/\partial x_3$  through the film  
46 thickness axis  $x_3$  where  $e_{33}$  is the piezoelectric stress coefficient expressed in Coulombs per  
47 square meter.

48 The EAR method is applied in this paper to piezoelectric polymer films of PVDF and  
49 PVDF-TrFE (polyvinylidene fluoride-trifluoroethylene). The measurement results of the  
50 electromechanical and electrical properties of PVDF films with three different thicknesses  
51 from 3 to 9  $\mu\text{m}$  are given, as well as their equivalent charge distribution along the thickness  
52 axis. The principle of the EAR method is first briefly described and details are given on the  
53 experimental set-up and the samples. Experimental results are presented and interpreted

54 in the light of known models. Then, the method used to isolate the electrical contributions  
 55 (permittivity and electric losses) and the mechanical contributions (coupling factor and me-  
 56 chanical losses) from the electrical measurement is explained. Finally, results and equivalent  
 57 charge distributions are presented and discussed before drawing conclusions.

## 58 **II. EAR METHOD, SET-UP AND SAMPLES**

### 59 **A. EAR principle**

60 Nondestructive direct space charge distribution measurement methods use the same prin-  
 61 ciple: the sample under test is perturbed from its electro-elastic equilibrium and thus gener-  
 62 ates a measurable signal when returning to equilibrium<sup>8</sup>. The perturbation can be initiated  
 63 by a thermal excitation (thermal method)<sup>9</sup>, an elastic excitation (pressure-wave-propagation  
 64 method or PWP)<sup>10</sup> or an electrical excitation (pulsed-electro-acoustic method or PEA)<sup>11</sup>.  
 65 Though thermal diffusion is a slow process and thus allows high spatial resolution to be  
 66 reached, the thermal method suffers from the evolution of the temperature profile during  
 67 the diffusion, which makes it difficult to recover the space charge distribution from measure-  
 68 ments. The inverse calculation to recover the space charge distribution is indeed an ill-posed  
 69 problem, hence noise may have a very large impact on the result reducing confidence in the  
 70 calculation. Concerning PWP and PEA methods, their implementation requires transfer  
 71 of elastic waves through at least one interface of the material under test to either excite it  
 72 (PWP) or obtain the signal (PEA). Therefore the mechanical conditions at the interfaces

73 and the spatial dispersion of any material defects make high spatial resolution difficult to  
 74 reach.

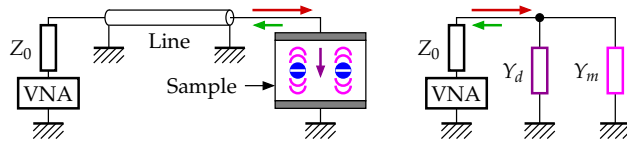


FIG. 1. (left) Sketch of the measurement setup. (right) Equivalent circuit. A Vector Network Analyzer (VNA) excites the sample (red arrows) at successive frequencies over a broad range through a line of impedance  $Z_0$ . Electric reflections from the sample (green arrows) depend on its dielectric properties (dark magenta) and elastic waves generated by the charges (light magenta). This is equivalent to a dielectric admittance  $Y_d$  in parallel with a mechanical admittance  $Y_m$ .

75 The EAR method (Electro-Acoustic Reflectometry) has been introduced to overcome  
 76 these problems<sup>12,13</sup>. This method is also based on the perturbation of the electro-elastic  
 77 equilibrium. The sample is electrically excited at successive frequencies distributed over a  
 78 broad frequency range (see Figure 1, red arrows). At each of these frequencies, the sample  
 79 consumes one part of the excitation energy (see Figure 1 in dark and light magenta) and  
 80 reflects back the other part (see Figure 1, green arrows). As the reflected part is the com-  
 81 plement of the consumed part, the measurement of the reflected part is an indirect way of  
 82 measuring the sample consumption. A large fraction of the consumed energy depends on  
 83 the dielectric properties of the sample and can be seen as an admittance  $Y_d$  (See Figure 1 in  
 84 dark magenta). A smaller fraction depends on the elastic waves generated by charges due to  
 85 the electrical excitation and can be seen as an additional electrical admittance  $Y_m$  in parallel  
 86 (see Figure 1 in light magenta). Thanks to mechanical resonances in the sample under test,

87 the reflected energy due to elastic waves appears in the signal as notches localized at given  
88 frequencies whereas the reflected energy due to dielectric properties evolves smoothly over  
89 the whole bandwidth. This makes it possible to isolate the reflected energy due to elastic  
90 waves from the one due to dielectric properties and thus to calculate independently the  
91 mechanical admittance  $Y_m$  and the dielectric impedance  $Y_d$ . As a consequence, information  
92 on both mechanical and dielectric properties of the sample are obtained. In addition, a  
93 reconstruction of the impulse response using the reflected energy due to elastic waves and  
94 an inverse Fourier transform allows a signal similar to the space charge distribution to be  
95 recovered as in the case of the PWP or PEA methods, space and time being connected by  
96 the velocity of sound. One advantage of the EAR method is that higher frequencies (so  
97 better spatial resolution) can be reached because excitation and measurement are directly  
98 made inside the sample (no interface to cross).

## 99 B. EAR set-up

100 The experimental set-up is pictured in Figure 2. At very high frequencies, propagation  
101 effects are no longer negligible and the use of a Vector Network Analyzer (VNA) with its  
102 probe station is the standard way to control and measure with great accuracy electrical  
103 reflections from the samples<sup>14</sup>. In this study, a ZNB40 VNA from Rohde&Schwarz and a  
104 station equipped with ACP RF probe from FormFactor were used to measure  $S_{11}$ , which is  
105 the electrical reflection coefficient from the sample under test. The whole set-up is calibrated  
106 by the Open-Short-Match procedure before measurements<sup>15</sup> using 106-683 calibration kit  
107 from FormFactor. This standard and precise calibration procedure allows losses and phasing



108 to be compensated at all frequencies caused by the propagation in cables and probe, and  
 109 ensures that measured  $S_{11}$  is the response of the sample only. The RF probe has 1-mm pitch  
 110 and 10-GHz bandwidth. The probe station is equipped with a binocular microscope and a  
 111 3-axis micrometer displacement stage to precisely place the probe signal tip on the sample  
 112 and the other probe tips on the ground plane (See inset in Figure 2).

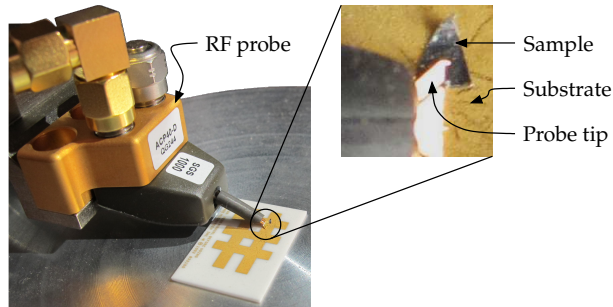


FIG. 2. The VNA is connected to an RF probe whose signal tip is in contact to one of the sample electrodes, the others being connected to ground through a golden substrate. The inset shows a larger view of the sample at the probe tip.

### 113 C. Samples and procedure

114 All piezoelectric samples are uni-axially oriented along the thickness axis. PVDF samples  
 115 were purchased from Solvay company. From the data-sheet, they are made of polycrystalline  
 116 PVDF polymer with crystalline domains in the  $\beta$ -phase<sup>16,17</sup>. They are 9- $\mu$ m thick and  
 117 aluminum coated on both sides. PVDF-TrFE samples were purchased from PolyK company.  
 118 From the data-sheet, this is a copolymerisation with 75% VDF and 25% TrFE. They are  
 119 5- $\mu$ m and 3- $\mu$ m thick and gold coated on both sides. All samples have a typical area of

120 slightly less than  $1 \text{ mm}^2$ . Their exact surface was determined from images for geometrical  
 121 factor compensation purposes.

122 Samples were placed on a commercial contact substrate covered with a highly conductive  
 123 golden copper plane that acted as ground plane. The measurements were carried out over a  
 124 bandwidth ranging from 20 MHz to 2.5 GHz with 500 kHz resolution.

### 125 III. EXPERIMENTAL RESULTS

#### 126 A. Measurements

127 The typical spectra showing the reflection coefficient amplitude  $|S_{11}|$  are presented for the  
 128 3 sample types in Figure 3. All  $|S_{11}|$  spectra show a base line varying slowly with frequency,  
 129 which corresponds to the dielectric response (permittivity and electrical losses) of the ma-  
 130 terial, on which various peaks appear. These peaks correspond to the additional energy  
 131 consumption resulting from the mechanical resonances due to the electro-elastic coupling.  
 132 The first resonance occurs at about 129 MHz for the  $9\text{-}\mu\text{m}$  thick PVDF sample, 198 MHz for  
 133 the  $5\text{-}\mu\text{m}$  thick PVDF-TrFE sample and 333 MHz for the  $3\text{-}\mu\text{m}$  thick PVDF-TrFE sample.  
 134 Due to symmetrical reasons and considering a uniform sample, the higher order resonances  
 135 correspond more or less to odd multiples of the fundamental frequency<sup>13</sup>. For PVDF-TrFE  
 136 samples however, some elastic resonances can be detected at even harmonics (see dotted  
 137 circles in Figure 3). This is an indication of a nonuniform material. Though mechanical  
 138 nonuniformities could generate resonances at even harmonics by themselves, they would  
 139 have a significant amplitude only if the mechanical nonuniformities were quite large thus

140 producing big mechanical mismatches. For apparent mechanically uniform materials, such  
 141 as those of the samples described in this paper, even harmonics are much more probably  
 142 produced by a nonuniform poling. This indeed breaks the sample symmetry, generating in  
 143 turn detectable even harmonics even for quite small nonuniform poling.

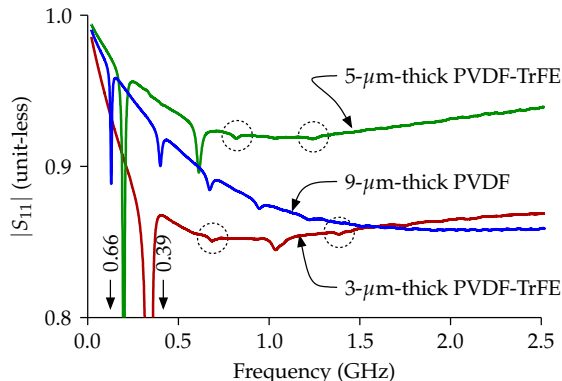


FIG. 3. Typical  $|S_{11}|$  measurement results for piezoelectric samples with different thicknesses. Only odd harmonics are detected with PVDF whereas odd and even harmonics (inside dotted circles) are present with PVDF-TrFE.

144 As electrical and mechanical responses can be seen as two impedances in parallel (see  
 145 Figure 1, right), it is preferable to study the sample admittance  $Y(\omega)$  as a function of  
 146 circular frequency  $\omega$  instead of  $S_{11}(\omega)$  directly obtained from raw measurements. One has

$$Y(\omega) = Y_0 \times \frac{1 - S_{11}(\omega)}{1 + S_{11}(\omega)}, \quad (1)$$

147 where  $Y_0 = 0.02 \text{ S} = 1/(50 \Omega)$  is the admittance of the VNA port.

148 Figure 4 presents the typical admittance for the 3 kinds of samples corrected from their  
 149 geometrical factor, *i.e.* multiplied by thickness over area. This corresponds to an equivalent  
 150 conductivity. The imaginary part is much larger than the real part and well proportional to

151 frequency which corresponds globally to a capacitive behavior. The real part corresponds to  
 152 the losses in the material. The mechanical resonances are visible and can be grossly modeled  
 153 by a series of RLC circuits (motion branches) in parallel with a capacitor (static branch) as  
 154 in the Butterworth Van Dyke electrical model<sup>18,19</sup>.

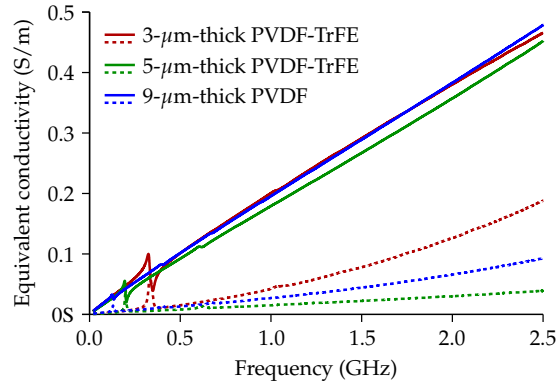


FIG. 4. Typical imaginary part (solid lines) and real part (dashed lines) of the admittance of the different kinds of samples corrected from their geometrical factor (equivalent conductivity). As expected a capacitive behavior is obtained on which resonances are visible.

## 155 B. Uniform material model

156 With thin samples compared to their diameter, elastic resonances originate only from the  
 157 thickness extension mode of vibration (TE mode). The admittance at resonance is a standard  
 158 way to extract the electro-mechanical properties of the material for the corresponding mode  
 159 of excitation, a method known as resonance method<sup>20</sup>. In the case of a uniform loss-less  
 160 piezoelectric material under free surface conditions, the admittance  $Y$  for the TE mode is

161 given by<sup>21</sup>:

$$Y(\omega) = \underbrace{j\omega C_0}_{Y_d} + \frac{j\omega C_0 k_{33}^2}{\underbrace{\frac{\omega d}{2v_s} \cot\left(\frac{\omega d}{2v_s}\right) - k_{33}^2}_{Y_m}} \quad (2)$$

162 where  $j^2 = -1$ ,  $C_0$  is the sample capacitance and  $d$  the sample thickness. The sample  
 163 capacitance is simply related to the permittivity at constant strain  $\epsilon_{33}^S$  by  $C_0 = \epsilon_{33}^S A/d$   
 164 where  $A$  is the sample area. Sound velocity  $v_s$  is related to the elastic stiffness coefficient at  
 165 constant electric displacement field  $c_{33}^D$  with the standard relation  $v_s^2 = c_{33}^D/m_v$ , where  $m_v$  is  
 166 the mass density. The coupling factor  $k_{33}$  is defined as the square root of the ratio between  
 167 stored and brought energies such that  $k_{33}^2 = e_{33}^2/(\epsilon_{33}^S c_{33}^D)$ <sup>22</sup>.

168 Equation (2) has two clearly identified terms: the first one corresponds to the static  
 169 capacitance (dielectric admittance  $Y_d$ ), and the second one corresponds to the different me-  
 170 chanical resonances of odd orders (mechanical admittance  $Y_m$ ). Since the  $Y_m$  is proportional  
 171 to  $Y_d$ , the impedance  $Z = 1/Y$  has also a convenient expression:

$$Z(\omega) = \frac{1}{j\omega C_0} \times \left( 1 - k_{33}^2 \frac{\tan\left(\frac{\omega d}{2v_s}\right)}{\frac{\omega d}{2v_s}} \right). \quad (3)$$

Dielectric and elastic losses can be respectively introduced through the loss tangent  $\tan \delta_d$   
 in the permittivity and the loss tangent  $\tan \delta_m$  in the elastic compliance so that

$$\epsilon^S \rightarrow \epsilon^S (1 - j \tan \delta_d) \quad \text{and} \quad c_{33}^D \rightarrow \frac{c_{33}^D}{1 - j \tan \delta_m}. \quad (4)$$

172 In the same way, the coupling factor experiences both kind of losses and becomes

$$k_{33}^2 \rightarrow k_{33}^2 (1 - j \tan \delta_d) (1 - j \tan \delta_m). \quad (5)$$

173 The complex admittance and impedance for a piezoelectric material with losses can then be  
 174 rewritten respectively as<sup>23</sup>

$$Y(\omega) = j\omega C_0 (1 - j \tan \delta_d) + \frac{j\omega C_0 (1 - j \tan \delta_d)^2 k_{33}^2}{\frac{j\omega d}{2v_s} (1 + j \frac{\tan \delta_m}{2}) \coth(\frac{j\omega d}{2v_s} (1 - j \frac{\tan \delta_m}{2})) - k_{33}^2 (1 - j \tan \delta_d)}, \quad (6)$$

175

$$Z(\omega) = \frac{1}{j\omega C_0 (1 - j \tan \delta_d)} - \frac{k_{33}^2 \tanh(\frac{j\omega d}{2v_s} (1 - j \frac{\tan \delta_m}{2}))}{j\omega C_0 \frac{j\omega d}{2v_s} (1 + j \frac{\tan \delta_m}{2})}. \quad (7)$$

176 As shown in<sup>23,24</sup>, the mechanical coupling factor  $k_{33}$ , the piezoelectric stress constant  
 177  $e_{33}$  and the mechanical loss tangent  $\tan \delta_m$  can be measured at first resonance frequency.  
 178 Therefore, the study of higher resonance orders allows the elastic properties to be accessed  
 179 on a broader spectrum range. In addition, by measuring the capacitance and the electrical  
 180 losses on the nonresonant part of the spectrum, the dielectric constant and the electrical  
 181 losses can be determined, knowing the sample geometrical factor.

182 Equations (6) and (7) describe very well the measurements insofar as the piezoelectric  
 183 material is uniform and its dielectric constant, losses and coupling factor have a sufficiently  
 184 slow evolution over the whole spectrum range. However, when the piezoelectric material is  
 185 no longer uniform, Expressions (6) and (7) can no longer directly be used.

### 186 C. Measurement analysis

187 In the case of actual measurements, at least for PVDF-TrFE samples, even harmonics are  
 188 present so (6) and (7) do not directly apply. With mechanical resonances showing localized  
 189 fast spectrum variations compared to dielectric behavior, it is relatively easy to isolate the  
 190 dielectric behavior from the measurements and thus extract  $C_0$  and  $\tan \delta_d$  from the base

191 line. Once done, these terms can be combined together with the impedance which leads,  
 192 supposing a uniform material, to

$$\frac{1}{1 - j \tan \delta_d} - j\omega C_0 Z(\omega) = k_{33}^2 \frac{\tanh\left(\frac{j\omega d}{2v_s} \left(1 - j\frac{\tan \delta_m}{2}\right)\right)}{\frac{j\omega d}{2v_s} \left(1 + j\frac{\tan \delta_m}{2}\right)}. \quad (8)$$

193 It is possible to decompose the second member of (8) as the sum of Lorentzian functions  
 194 since

$$\frac{\tanh(jw(1 - j\zeta))}{jw(1 + j\zeta)} = \frac{1}{1 + \zeta^2} \sum_{k=0}^{\infty} \frac{2}{\left(\frac{k\pi + \pi/2}{1 - j\zeta}\right)^2 - w^2}, \quad (9)$$

195 where  $w$  is a reduced circular frequency, here  $w \equiv \frac{\omega d}{2v_s}$ , and  $\zeta$  is a loss factor, here  $\zeta \equiv \frac{\tan \delta_m}{2}$ .

196 As a consequence, each maximum in (8) can be reasonably assumed associated with a single  
 197 normalized Lorentzian function  $L(w)$ , defined as

$$L(w) = \frac{2j\alpha w_R^2}{w_R^2 + 2j\alpha w_R^2 - w^2}, \quad (10)$$

198 with

$$\begin{cases} w_R = \frac{\sqrt{1 - \zeta^2}}{1 + \zeta^2} \times (k\pi + \pi/2) \\ \alpha = \frac{\zeta}{1 - \zeta^2} \end{cases} \quad (11)$$

199 since (9) can be rewritten as

$$\frac{\tanh(jw(1 - j\zeta))}{jw(1 + j\zeta)} = \frac{1}{1 + \zeta^2} \sum_{k=0}^{\infty} \frac{L(w)}{j\alpha w_R^2}. \quad (12)$$

200 The natural circular frequency  $w_R$  allows  $v_s$  to be determined and damping factor  $\alpha$  allows  
 201  $\tan \delta_m$  to be determined. The square of the coupling coefficient  $k_{33}^2$  is directly obtained from  
 202 the magnitude of the normalized Lorentzian function peak multiplied by  $(1 + \zeta^2) \alpha w_R^2$ . This  
 203 is pushed further to nonuniform materials in the following subsections.

204 **1. Dielectric properties**

205 Figure 5 shows the relative permittivity and  $\tan \delta_d$  as a function of frequency. This  
 206 information is obtained from the admittance taking into account geometrical factors and  
 207 canceling resonances by appropriate Lorentzian functions. As a small residual may remain  
 208 in the cancellation (see inset in Figure 5), a smoothing is applied. It consists in replacing  
 209 by a spline function the part of the curve that includes the residual.

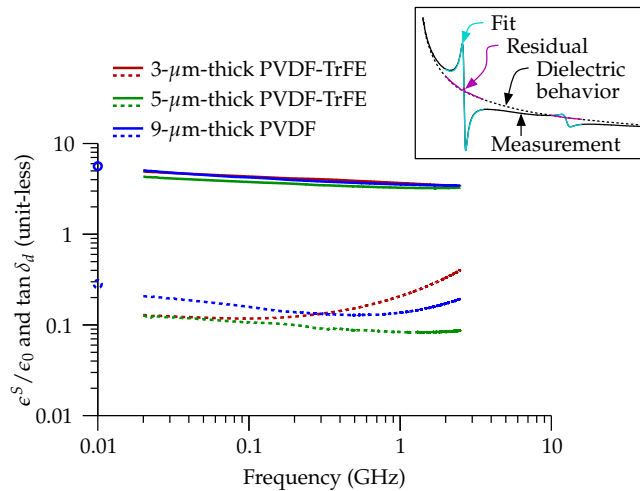


FIG. 5. Typical relative permittivity  $\epsilon^S/\epsilon_0$  (solid lines) and dielectric losses  $\tan \delta_d$  (dashed lines) of the different kinds of samples. The circles on the  $y$ -axis correspond to the higher frequency values obtained from<sup>25</sup>. In the inset, mechanical resonance fits on a measurement and residual smoothing to obtain the material dielectric behavior.

210 Relative permittivity  $\epsilon^S/\epsilon_0$ , where  $\epsilon_0$  is the vacuum permittivity, reduces regularly on the  
 211 frequency range from about 5 to about 3.5. Losses experience similar trend at low frequency  
 212 but increase rapidly at higher frequency. PVDF has a higher  $\tan \delta_d$  than PVDF-TrFE at  
 213 low frequency (60% larger). Compared to 5- $\mu\text{m}$ -thick PVDF-TrFE, the cutoff frequency of



214 9- $\mu\text{m}$ -thick PVDF is much lower, slightly under 1 GHz. The comparison of PVDF-TrFE  
215 samples shows a rapid increase of losses for the thinner sample, probably due to the film  
216 processing which may be less efficient in the case of thinner materials. This is also visible  
217 in the relative permittivity since the one of the 5- $\mu\text{m}$ -thick sample is 15% lower.

218 All the measurements are consistent with the ones reported in<sup>23,24</sup> using resonant meth-  
219 ods. The measured relative permittivity at high frequency is much lower than the one at  
220 very low frequency (dc value) since a value between 10 and 13 is generally reported for  
221  $\beta$ -PVDF. For instance in<sup>25</sup> the evolution of relative permittivity and  $\tan \delta_d$  was measured  
222 between 100 Hz and 10 MHz for PVDF films with different crystalline properties. Rela-  
223 tive permittivity reaches 13 for  $\beta$ -PVDF below 100 kHz and decreases monotonically to 5  
224 at 10 MHz. Concerning  $\tan \delta_d$ , it starts from 0.03 at 100 Hz and reaches as high as 0.3  
225 around 2.5 MHz and begins to decrease slowly above. This is consistent with the transition  
226 of relative permittivity around 1 MHz<sup>26</sup> and the decrease continues reaching about 0.13 at  
227 500 MHz.

228 The increase of  $\tan \delta_d$  at higher frequency can be attributed to another effect since no  
229 relative permittivity variation is observed. The contact resistance at the electrodes can  
230 indeed enter into consideration. The same applies to the 3- $\mu\text{m}$ -thick PVDF-TrFE sample.

231 The general behavior of relative permittivity and  $\tan \delta_d$  as a function of frequency is  
232 well described by Xia and Zhu<sup>5,26</sup>. The observed variations at low frequencies correspond  
233 to different polarization processes in polymers that are too slow to contribute at higher  
234 frequencies. Therefore, in sub-gigahertz and gigahertz ranges, the relative permittivity and  
235  $\tan \delta_d$  decrease with frequency.

236 **2. *Electro-mechanical properties***

237 Using the combination in the left member of (8), Lorentzian functions (10) can be fitted  
 238 on each resonance. Results are reported and interpreted for each material in tables I, II and  
 239 III. Velocity  $v_s$ , mechanical loss  $\tan \delta_m$  and coupling coefficient  $k_{33}$  are obtained from

$$\left\{ \begin{array}{l} v_s = \frac{2df_R}{N} \frac{1 + \zeta^2}{\sqrt{1 - \zeta^2}} \\ \tan \delta_m = 2\zeta \\ k_{33} = \frac{2}{\pi N} \sqrt{M\zeta \frac{1 + \zeta^2}{1 - \zeta^2}} \end{array} \right. \quad (13)$$

240 where  $f_R$  is the resonance frequency of the harmonic of order  $N$ , and  $M$  is the magnitude  
 241 of the Lorentzian (10) to fit the resonance.

242 Velocity does not significantly vary with frequency, being about 2420 m/s for PVDF  
 243 and 2050 m/s for PVDF-TrFE. Mechanical losses  $\tan \delta_m$  are quite similar for all materials,  
 244 typically  $\tan \delta_m = 0.05$ , slightly better for the 5- $\mu\text{m}$ -thick PVDF-TrFE than other sam-  
 245 ples, emphasizing further a better process control for this material thickness. The coupling  
 246 coefficient is much larger for PVDF-TrFE (about 0.25, which corresponds to the manufac-  
 247 turer value) than for PVDF (0.166, which is close to the standard value for  $\beta$ -PVDF<sup>23,24</sup>).  
 248 However  $k_{33}$  decreases more rapidly with PVDF-TrFE than with PVDF. For high harmonic  
 249 orders, PVDF has therefore a better coupling. This variation of the coupling coefficient has  
 250 already been reported in<sup>27</sup> for piezoelectric thin films resonators made of aluminum nitride  
 251 (AlN) and lead zirconate titanate (PZT). Early studies on PVDF<sup>28</sup> on a much narrower  
 252 frequency range have also reported the slight decreasing of  $k_{33}$  as a function of frequency.

TABLE I. (upper part) Lorentzian parameters (resonance frequency  $f_R$ , loss factor  $\zeta$  and magnitude  $M$ ) for the 9- $\mu\text{m}$ -thick PVDF sample and (lower part) deduced mechanical characteristics (sound speed  $v_s$ , mechanical losses  $\tan \delta_m$  and coupling coefficient  $k_{33}$ ) for each detectable harmonic order. Unit-less when not specified.

Order $N$	1st	3rd	5th	7th	9th
$f_R$ (MHz)	131.0	400.5	671.5	945.0	1224.0
$\zeta$	0.0339	0.0257	0.0240	0.0219	0.0204
$M$	0.3307	0.0407	0.0141	0.0058	0.0025
$v_s$ (m/s)	2362	2405	2419	2432	2450
$\tan \delta_m$	0.0678	0.0514	0.0480	0.0438	0.0408
$k_{33}$	0.166	0.152	0.145	0.124	0.100

### 253 3. Equivalent charge distribution

254 Equivalent charge distribution corresponds to the opposite of the divergence of the dipole  
 255 distribution for piezoelectric materials. In the case of uniform piezoelectric materials, equiv-  
 256 alent charges appear only at the sample boundaries, positive on one side and negative on the  
 257 other side. In the case of a nonuniform piezoelectric material, additional equivalent charges  
 258 appear inside the sample, that is to say between the charges at the boundaries.

259 The equivalent charge distribution can be well estimated with the EAR method from  
 260 the inverse Fourier transform of the mechanical resonances which are characterized by the

TABLE II. (upper part) Lorentzian parameters (resonance frequency  $f_R$ , loss factor  $\zeta$  and magnitude  $M$ ) for the 5- $\mu\text{m}$ -thick PVDF-TrFE sample and (lower part) deduced mechanical characteristics (sound speed  $v_s$ , mechanical losses  $\tan \delta_m$  and coupling coefficient  $k_{33}$ ) for each detectable harmonic order. Unit-less when not specified.

Order $N$	1st	3rd	4th	5th	6th
$f_R$ (MHz)	203.0	612.0	813.5	1010.0	1237.5
$\zeta$	0.0240	0.0240	0.0282	0.0355	0.0245
$M$	0.9171	0.0413	0.0036	0.0018	0.0024
$v_s$ (m/s)	2032	2042	2036	2024	2064
$\tan \delta_m$	0.0480	0.0480	0.0564	0.0710	0.0491
$k_{33}$	0.233	0.148	0.063	0.063	0.072

261 set of Lorentzian functions described in Section III C<sup>13</sup>. Since the lateral dimensions of the  
 262 samples are much larger compared to their thickness, the plane wave approximation applies  
 263 and the time axis in the inverse Fourier transformation (impulse response) is comparable to  
 264 the position in depth knowing the velocity of sound. Figure 6 shows such inverse Fourier  
 265 transformations for the three kinds of samples. Zero padding is used to obtain a sufficient  
 266 time resolution.

267 For the 9- $\mu\text{m}$ -thick PVDF sample, the equivalent charges are well localized at the sam-  
 268 ple boundaries, *i.e.* no significant equivalent charge is detected inside the sample. This  
 269 corresponds to a uniformly poled material because the changes in piezoelectric coefficient

TABLE III. (upper part) Lorentzian parameters (resonance frequency  $f_R$ , loss factor  $\zeta$  and magnitude  $M$ ) for the 3- $\mu\text{m}$ -thick PVDF-TrFE sample and (lower part) deduced mechanical characteristics (sound speed  $v_s$ , mechanical losses  $\tan \delta_m$  and coupling coefficient  $k_{33}$ ) for each detectable harmonic order. Unit-less when not specified.

Order $N$	1st	2nd	3rd	4th	5th
$f_R$ (MHz)	346.5	674.5	1025.5	1387.5	1747.5
$\zeta$	0.0309	0.0417	0.0245	0.0178	0.0427
$M$	0.8646	0.0051	0.0113	0.0031	0.0057
$v_s$ (m/s)	2082	2029	2053	2082	2103
$\tan \delta_m$	0.0618	0.0834	0.0491	0.0356	0.0853
$k_{33}$	0.257	0.046	0.078	0.047	0.123

270 between the inside and the outside of the sample are well localized at the sample boundaries.  
 271 However, for both PVDF-TrFE samples, equivalent charges are clearly detected inside the  
 272 material, as shown in the dotted circles in Figure 6. This indicates that  $e_{33}$  is larger in the  
 273 middle of the sample than at its boundaries since the piezoelectric coefficient changes are  
 274 more progressive. This result confirms the assumption raised from the detection of even  
 275 harmonics, already detected in the  $S_{11}$  spectra shown in Figure 3, and gives in addition the  
 276 location of these nonuniformities.

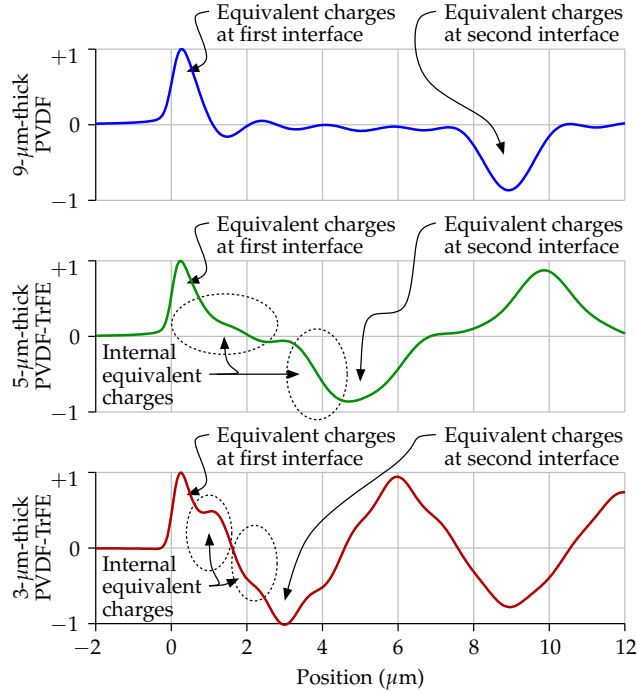


FIG. 6. Equivalent charge distribution for the different samples as a function of position: PVDF 9 $\mu\text{m}$ -thick (blue), PVDF-TrFE 5 and 3  $\mu\text{m}$ -thick (green and red). A uniform material presents only opposite equivalent charges at the material boundaries (indicated here as first and second interfaces). This is actually the case for the PVDF sample but not for both PVDF-TrFE samples which present additional equivalent charges inside the material (dotted circles) indicating a variation of the piezoelectric coefficient as a function of depth.

#### 277 IV. CONCLUSION

278 In this work, dielectric and electromechanical properties of PVDF and PVDF-TrFE piezo-  
 279 electric materials have been determined over a very broad frequency range, up to above the  
 280 gigahertz. This extends above 10 MHz already reported results.

281 The Electro-Acoustic-Reflectometry (EAR) method has been used for all measurements.  
 282 Information was extracted from measurements by fitting mechanical resonances with ap-

283 appropriate Lorentzian functions. This makes the distinction of dielectric and mechanical  
284 responses possible and thus the extraction of dielectric and mechanical properties of the  
285 tested piezoelectric film. In addition the film poling uniformity can be obtained.

286 It is found that tested PVDF-TrFE samples are not uniformly poled compared to PVDF.  
287 Their piezoelectric coefficient is actually found larger in the middle of the material which  
288 generates even modes of resonance when excited. In addition, the conductivity of electrodes  
289 seems to impact the material efficiency at higher frequency.

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