Simultaneous determination of the mechanical moduli and mass of thin layers using nonadditive quartz crystal acoustic impedance analysis

Roberto Etchenique and Ariel Dan Weisz

INQUIMAE, Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, AR 1428 Buenos Aires, Argentina

(Received 18 January 1999; accepted for publication 26 April 1999)

High frequency rheological properties of polymer films have been measured using a nonadditive quartz crystal resonator impedance approach. The method involves fast measurement of the quartz covered with the film in contact with solutions of different viscosities and the measurement of the equivalent impedance of the bare quartz resonator in contact with the same solutions. Although by using a standard quartz crystal acoustic impedance method it is not possible to determine more than two of the four film parameters (density, thickness, storage modulus $G'$, and loss modulus $G''$), we demonstrate that the interaction between the film under study and a semi-infinite layer of liquid gives the additional information needed to get the mechanical moduli $G'$ and $G''$ simultaneously with the mass or thickness of the film. An alternative approach to measure $G'$ and $G''$, which involves independent and very precise determination of the film thickness, is discussed. Experimental measurements of polystyrene using dioctyl phthalate as a plasticizer show excellent agreement with Martin’s model for quartz resonators covered with viscoelastic nonpiezoelectric layers. The results demonstrate that quartz resonators can be used to measure high frequency rheological properties of films simply without the need of an independent measurement of thickness.

© 1999 American Institute of Physics. [S0021-8979(99)07315-6]

INTRODUCTION

Shear mode quartz resonators are being widely used to measure the viscoelastic properties of materials such as polymers, molecular composites, gels, etc. As early as 1949, Mason et al. used a cylindrical quartz crystal to probe the viscoelastic properties of polymer solutions. A decade later, Sauerbrey described the general dependence of the resonance frequency of a quartz crystal resonator as a function of the deposited mass of a metal in vacuum.

Despite the general opinion that a quartz crystal resonator could not oscillate if put in contact with a highly damped medium such as a liquid, several works have demonstrated that oscillations were possible even in viscous media.

The immediate application was the use of transverse shear mode devices as microgravimetric devices (quartz crystal microbalances) which are capable of nanogram detection in mass changes of rigid materials.

However, if the surface film is not entirely rigid, the quartz crystal response depends not only on the mass but also on the viscoelastic properties of the attached layer.

Various authors have considered the effect of nonrigid coupling in the context of studies of polymers deposited on surfaces. Muramatsu et al. used the resonant resistance in addition to the resonant frequency of the quartz crystal microbalance (QCM) as a criterion to evaluate film nonrigidity for several polymer systems, including poly(pyrrrole), Nafion®, Langmuir–Blodgett, and other films. To part

$\text{Nafion}^\circledast$ and $\text{Langmuir–Blodgett}$

and Noel reported in situ monitoring of viscoelastic volume and mass changes during electrochemical growth and redox switching of poly(pyrrrole) modified electrodes by simultaneously recording the damping resistance, charge, and resonant frequency of the quartz resonator. Hillman and co-workers applied dynamic quartz crystal impedance measurements to modified electrodes to study film growth and redox switching by qualitative analysis of the width of the acoustic admittance-frequency peak. Oyama and co-workers measured the resonant frequency and resonant resistance of quartz crystal resonators coated with several redox active polymers, DNA, and tungsten oxide. A detailed study of the electroacoustic impedance analysis of a quartz crystal oscillator was presented by Frubose, Dobhoffer, and Soares in a study of the viscoelastic properties of overlayers. Johannsmann et al. and Katz and Ward have reported the use of quartz crystal electrical impedance to study the viscoelastic properties polymer thin films.

Some studies of high frequency shear viscoelastic liquids have been reported by Tozaki et al. and by Kanazawa and co-workers using the QCM. The viscoelastic properties of polymer solutions, gels, and grafted polymer layers were investigated using the QCM at 9 MHz by Ivanchenko et al.

Several theoretical approaches to the viscoelastic layer problem were made. Reed et al. derived a relationship between the complex admittance of the coated quartz resonator and the mass, density, and complex shear modulus $G = G' + jG''$ of the deposited material. Granstaff and Martin reported a completely equivalent equation, and extended the...
analytical results to a bilayer. Lucklum et al.\textsuperscript{32} extended the model for a multilayer system.

In this article we use Martin’s model\textsuperscript{31} to describe the variation of the resonant properties of the quartz substrate due to the changes in density, thickness, storage modulus, and loss modulus of a deposited layer. Impedance polar parametric plots are introduced to analyze the effect of these rheological changes in the quartz resonance. Calvo et al.\textsuperscript{33} demonstrated that a maximum of two parameters can be derived from admittance QCM measurements, i.e., for a given density, measurements of the thickness and of both modulus components are impossible to achieve, and artifacts are obtained if at least one of the three magnitudes is not independently known.

We further introduce a second layer (overlayer) in contact with the first layer (underlayer) and describe the behavior of the crystal resonance in terms of the variation of the viscosity of the overlayer. We show that the change in the resonance properties due to variation in the overlayer viscosity can be used to obtain information about the rheology of the underlayer and more than two parameters can be obtained.

We discuss the application of Martin’s model for the measurement of viscoelastic properties of polymer films. Experimental data obtained from dioctyl phthalate doped polystyrene films are found to be in excellent agreement with the theoretical model.

**QUARTZ RESONATOR IMPEDANCE**

The mechanical properties of the quartz resonator can be described in terms of an electrical equivalent circuit. Figure 1 shows the widely used Butterworth–Van Dyke (BVD) model,\textsuperscript{34} in which the inertial mass of the quartz is represented by the inductance, \( L_Q \), the quartz compliance by the capacitance, \( C_Q \), and the mechanical damping by the resistance, \( R_Q \). These three equivalent components describe the motional branch of the equivalent circuit. An additional capacitance, \( C_0 \), represents the parasitic electrical capacitance of the wires, connections, holder, and the quartz crystal itself and has no mechanical equivalence.

When nonpiezoelectric layers are attached to the quartz resonator, the equivalent parameters change. We define the equivalent electrical impedance of the quartz resonator as \( Z_Q = R_Q + j\omega L_Q = R_Q + X_{L_Q} \). If the impedance of the quartz resonator \( Z_Q \) is very high compared with the nonpiezoelectric layer impedance \( Z_1 = R_1 + X_{L_1} \), the total electrical equivalent impedance of the system can be approximated as \( Z = Z_Q + Z_1 \).\textsuperscript{10}

Granstaff and Martin\textsuperscript{31} have derived an expression for the electrical equivalent impedance \( Z \) in terms of the mechanical impedance \( Z_M \).

\[
Z = \frac{2\omega L_Q}{\pi \sqrt{\mu_Q \rho_Q}} Z_M = R_M + jX_{LM},
\]

(1)

with

\[
L_Q = \frac{h_Q^3}{8\pi e_{26}},
\]

where \( \mu_Q = 2.957 \times 10^{10} \text{ N m}^{-2} \) is the elastic constant for piezoelectrically stiffened quartz, \( \rho_Q = 2650 \text{ Kg m}^{-3} \) is the density of the quartz, \( h_Q \) is the thickness of the quartz, \( A \) is the active area of the gold electrode, and \( e_{26} = 9.652 \times 10^{-2} \text{ C m}^{-2} \) is the quartz piezoelectric stress constant.

The properties of the nonpiezoelectric layer are represented by its mechanical impedance\textsuperscript{31}

\[
Z_M = \sqrt{\rho Q G} \tanh(kd),
\]

(2)

where \( G = G' + jG'' \) is the complex shear modulus of the nonpiezoelectric layer, \( k = j\omega \sqrt{\rho Q G} \), the wave propagation constant, and \( d \) the thickness of the nonpiezoelectric layer of density \( \rho \).

If the layer is thick enough \( (d \to \infty) \), the shear wave vanishes in the bulk of the layer, and no energy is transferred from this point. In this case, \( \tanh(kd) \to 1 \) and \( Z_M = Z_M = \sqrt{\rho Q G} \), where the superscript \( ^{(\ast)} \) indicates the semi-infinite approximation.

If the layer is very thin \( (d \to 0) \) or the modulus of the material is high \( (G \to \infty) \), the entire layer oscillates in phase and no energy is lost. In this case, \( \tanh(kd) \to kd \) and \( Z_M = X_{LM} = j\omega \rho Q m/A \). The resistive part of \( Z \) is zero, and its inductive part shifts the resonance to lower frequencies, depending on the areal mass density of the layer.

For small changes in \( X_{LM} \), corresponding to a low deposited mass, the variation in resonant frequency can be approximated as linear on \( X_{LM} \), and the Sauerbrey equation,

\[
\Delta f_0 \approx \frac{-2f_0^2}{\sqrt{\mu Q \rho Q}} \frac{\Delta m}{A},
\]

(3)

is obtained,\textsuperscript{3} where \( A \) is the active area of the piezoelectric resonator and \( \Delta m \) is the variation in the electrode mass. Metal layers and other rigid materials often fulfill this condition.

Note that the expressions for mechanical and electrical impedance differ only in the factor \( 2\omega L_Q/\pi \sqrt{\mu Q \rho Q} \); therefore all the relationships encountered for mechanical impedances are also valid for their electrical equivalents [Eq. (2)].

If two nonpiezoelectric layers are successively attached to the crystal, the following expression applies:

\[
Z = \frac{Z_1^2 \tanh(k_1 d_1) + Z_2^2 \tanh(k_2 d_2)}{1 + \frac{Z_2^2}{Z_1^2} \tanh(k_1 d_1) \tanh(k_2 d_2)},
\]

(4)

where the subscript 1 refers to the underlayer and the subscript 2 to the overlayer.\textsuperscript{31}
If the mechanical interaction between both layers is negligible, the denominator tends towards unity and additivity holds, that is, \( Z = Z_m^\infty \tanh(k_d d_1) + Z_q^\infty \tanh(k_d d_2) \).

This is normally the case for a thin and rigid underlayer immersed in a liquid (a semi-infinite overlayer). If the viscosity and density of the liquid are kept constant, the impedance of the underlayer can be obtained by subtraction.

For the case of two layers with similar softness (two similar rubbery polymers, a gel covered with water, etc.) the interaction between both layers is not negligible and Eq. (4) must be used.

**MATERIALS AND METHODS**

All the measurements were performed using a QCM cell made totally of acrylic. The polished 14 mm gold coated AT cut quartz crystals that were employed were purchased from ICM Company Inc., Oklahoma City, OK. The crystals were mounted into the cell by sealing nitrile O rings with only one face in contact with the liquid and/or polymer films. The active area of the gold electrodes is \( A = 0.196 \text{ cm}^2 \) and the thickness of the quartz is \( h_Q = 0.168 \text{ mm} \). A rotating glass rod was used to keep the solutions under continuous stirring. The QCM setup is described elsewhere.\(^{33}\)

Di(ethylene glycol) 99\%, (Aldrich) was used without further purification. The polymer solution was prepared as follows: 1 g polystyrene (Aldrich) on MW 280.000, \( \rho = 1.047 \text{ g cm}^{-3} \), and 30 mg dioctyl phthalate 99\% (Aldrich) were dissolved in 10 ml toluene. All chemicals used were analytical grade. Thin films of doped polystyrene were deposited onto the crystal by solvent evaporation. All measurements were performed at room temperature (23°C).

**CRYSTAL IMPEDANCE MEASUREMENT METHOD**

Figure 2(a) shows the measuring circuit consisting of an ac voltage divider formed by a quartz resonator impedance \( Z_q \) and the measuring capacitor \( C_m \). A sinusoidal signal (10 mV pp) generated by a computer controlled variable frequency oscillator (VFO) is applied to the input of the transference voltage divider.\(^{35}\)

A sawtooth voltage was applied with a 12 bit digital/analog (D/A) converter attached to a 486 computer to the VFO to perform a frequency linear sweep. The sweep frequency limits were measured with an on-board frequencimeter also connected to the computer.

Both the input \( V_i \) and output \( V_o \) were amplified, rectified, and measured with a 12 bit A/D board attached to a 486 computer. The sample rate was 50 complete spectra per second, each containing 100 measured points as can be seen in Fig. 2(b). The data acquisition software was written in Basic.

The ratio of the output to input ac voltage for the transference voltage divider is

\[
\frac{V_o}{V_i} = \left(1 + \frac{Z_m}{Z_q}\right)^{-1}, \tag{5}
\]

where \( Z_m \) is the measuring impedance and \( Z_q \) is the electrical impedance of the quartz resonator at the frequency \( \omega \). In terms of a BVD circuit, \( Z_q \) is given by

\[
Z_q = \frac{L}{C_o} - \frac{1}{\omega^2 C_0} \frac{j R}{\omega C_0} \frac{1}{R + j \omega L - \frac{j}{\omega} \left(\frac{1}{C} + \frac{1}{C_0}\right)}. \tag{6}
\]

Substitution of Eq. (6) in Eq. (5) gives the following expression for the absolute value of the voltage divider transfer function spectrum:

\[
\left|\frac{V_o}{V_i}\right| = \left\{\left[\omega L - \frac{1}{\omega C} \right]^2 + R^2\right\}^{1/2} \left[\omega L - \frac{1}{\omega C} + \frac{\omega L C_0}{C} - \frac{1}{\omega C_0} \right]^2 \left[\frac{R + \frac{R C_0}{C_0}}{C_0}\right]^2 \right\}^{1/2}. \tag{7}
\]

BVD equivalent parameters \( R, L, \) and \( C_0 \) were obtained by a least square fit of Eq. (7) to the measured data. The fitted values for \( L = L_Q + L_f \) and \( R = R_Q + R_f \) represent the total equivalent impedance of the covered quartz.

The contribution of the nonpiezoelectric film, \( R_f \) and \( L_f \), can be obtained by subtraction of the parameters of the bare quartz. Since \( C \) represents the quartz crystal compliance and is not expected to vary in the experimental conditions, a fixed value of \( C \) was used according to the criterion proposed by Martin et al.\(^{10}\)

The solid line in Fig. 2(b) corresponds to a nonlinear fit of Eq. (7) to the experimental points with \( C = 3.36 \text{ fF}, R = 216.3 \Omega, L = 7.5052 \text{ mH}, \) and \( C_0 = 8.5 \text{ pF} \), where the
bare crystal parameters are $C_Q=3.36 \, \text{fF}$, $R_Q=26.2 \, \Omega$, $L_Q=7.5029 \, \text{mH}$, and the film equivalent parameters are $R_f=190.1 \, \Omega$ and $L_f=3.11 \, \mu\text{H}$.

**RESULTS AND DISCUSSION**

In order to allow a direct comparison of the resistive and inductive components of the film impedance we use $X_{L_f} = j\omega L_f$ rather than $L_f$.

Figure 3 shows the variation of $X_{L_f}$ and $R_f$ for a polystyrene film with 3% mass dioctyl phthalate as a plasticizer when the temperature is varied. At low temperatures (10 °C) the film behaves as a rigid material, as can be deduced from the low value of $R_f$ if compared with $X_{L_f}$. A value of $X_{L_f}=3757 \, \Omega$ corresponds to a frequency shift of 39 860 Hz which represents a deposited mass of 178 $\mu\text{g}$ under the Sauerbrey approximation or by using the Behrndt method.

$R_f$ increases monotonously with temperature, indicating softening of the film. The hysterisis in $X_{L_f}$ during the temperature cycle is within 0.3%, showing that the film mass does not vary during the experiment as expected from the low vapor pressure of the film components. Therefore, the major changes in $X_{L_f}$ and $R_f$ are due to a decrease in $G'$ and/or $G''$ when the temperature is raised.

Assuming a constant density of the film, an initial attempt to obtain the values of $G'$ and $G''$ at each temperature was made. The thickness $d$ of the film was estimated assuming the Sauerbrey limit, using the values of $X_{L_f}$. Note that the variation of $X_{L_f}$ between the temperature limits is below 4%.

The values of $G'$ and $G''$ that satisfy Eq. (2) for each point described by the three parameters, $X_{L_f}$, $R_f$, and $d$, were found by means of a simplex algorithm with error $\epsilon < 0.1 \, \Omega$ for $R_f$ and $X_{L_f}$, which is below the resolution of the experimental measurement under the conditions described. Figure 4 shows the $G'$ and $G''$ obtained as previously described for the cooling process from 100 to 10 °C. The parametric Cole–Cole representation of $G''$ vs $G'$ is shown in curve (a) of Fig. 5. Although this plot seems to be in excellent agreement with a single relaxation process, it is an artifact, produced due to a wrong estimation of the thickness. Curve (b) in Fig. 5 shows the Cole–Cole plot for the same experimental data shown in Fig. 3, but in this case the values of $G'$ and $G''$ were obtained using thickness values 1% below the ones used for the first estimation. Note that a small uncertainty in the determination of $d$ produces a dramatic change in the calculated $G'$ and $G''$. Different Cole–Cole semicircles can be obtained using slightly different values of the thickness $d$. The noise in raw data ($R_f$ and $X_{L_f}$) is translated to this pseudo-Cole–Cole representation as scattering in the angle from the center of the semicircle, as can be seen by a comparison of Figs. 4 and 5. Even for pure Newtonian behavior, with $G'=0$ and a finite $G''$ variation, the artifact appears, as was previously demonstrated.

To perform the measurement of both $G'$ and $G''$ without independent and very precise knowledge of $d$, we need a new observable magnitude. Equation (4) shows that, for the general case of two viscoelastic layers, the values of each $Z_f$ are not additive. For materials with values close to $Z_f$ when measured separately, the dependence of $Z_f$ on the overlayer viscosity will be perturbed by the properties of the underlayer if measured as a whole system.

A bare quartz crystal was mounted into the cell and its equivalent impedance was measured. Values of $R_f$ and $X_{L_f}$ are always obtained by subtraction of $R_Q$ and $X_{L_Q}$, the parameters for the bare quartz resonator. Immediately, 1 ml of water was poured into the cell and a new impedance was

---

**FIG. 3.** Parametric polar plot of the thermal cycle for a polystyrene-dioctylphthalate film. The $X_{L_f}$ axis is shifted to preserve the scale.

**FIG. 4.** $G'$ and $G''$ obtained by fitting Eq. (2) to the experimental data in Fig. 3 for the cooling process from 100 to 10 °C. The thickness was evaluated from the Sauerbrey equation and a constant density $\rho=1.047 \, \text{g cm}^{-3}$.

**FIG. 5.** (a) Polar Cole–Cole representation of the data in Fig. 4. (b) Cole–Cole plot of the moduli data obtained in the curve in (a) but using a 1% lower value for the thickness $d$. 

---
FIG. 6. (a) Successive additions of solutions of increasing viscosity (DEG-H2O) to one side of the bare crystal. (b) The same as in (a) except the crystal is covered with a thin (~350 nm) polystyrene-dioctylphthalate film. (c) The same as in (a) except the crystal is covered with a medium (~600 nm) polystyrene-dioctylphthalate film. (d) The same as in (a) except the crystal is covered with a thick (~900 nm) polystyrene-dioctylphthalate film.

registered. Successive 100 µl aliquots of the liquid in the cell were replaced by diethylene glycol (DEG) to obtain solutions of increasing viscosities $\eta_{LIQ}$. The entire procedure was done while stirring to facilitate fast mixing and equilibration of the solutions. Impedance data for all of the procedure are shown in Fig. 6(a). Note that $\Delta R_f$ and $\Delta X_{LIQ}$ are very close, which corresponds to a semi-infinite liquid layer with negligible elasticity ($G_{LIQ}' \approx 0$ and $G_{LIQ}'' = \omega \eta_{LIQ}$) as can be expected for DEG solutions. The same protocol was followed for quartz crystals coated with three films of different thickness. The experimental data are shown in Figs. 6(b)–(d).

While for the bare crystal $\Delta R_f \approx X_{LIQ}$, for the coated quartz resonators the $\Delta R_f$ values are significantly higher than $\Delta X_{LIQ}$. This gives slopes for $R_f$ vs $X_{LIQ}$ that are higher than unity as can be seen in Fig. 7 (shown by dots).

According Eq. (2) and assuming semi-infinite behavior for the solution layer ($d_{LIQ} \to \infty$)

$$Z_{LIQ} = Z_{LIQ}^* = \sqrt{\rho_{LIQ} G_{LIQ}}.$$ (8)

Similarly, for the film in air, not in contact with the liquid overlayer

$$Z_f = Z_f^* \tanh(k_fd_f)$$ (9)

with

$$Z_f^* = \sqrt{\rho_f G_f},$$

where $Z_f^*$ is the impedance of a very thick (infinite) layer of the coating.

For the coated quartz covered with the solution, we use nonadditive Eq. (4). Subscript $f$ denotes the polystyrene underlayer. The overlayer, if any, is the DEG solution.

$$Z_{LIQ}^* = \frac{Z_f^*}{Z_f^*} \tanh(k_fd_f) + Z_{LIQ}^*.$$ (10)

Combining Eq. (8)–(10), and extracting the modulus and angle we obtain

$$\tanh(k_fd_f) = \frac{Z^*_{air}}{Z^*_{f}}.$$ (11)

$$Z_{LIQ}^* Z_{air}^* = Z_f^* 2 \left( \frac{Z^*_{air} + Z_{air}^* - Z_{LIQ}^*}{Z_f^*} \right),$$ (12)

$$|Z_{LIQ}^*| = \left| Z_f^* \frac{|Z^*_{air} + Z_{air}^* - Z_{LIQ}^*|}{|Z_f^*|} \right|,$$ (13)

$$2 \arg Z_f^* = \arg Z_{air}^* + \arg Z_{LIQ}^* - \arg(Z^*_{air} + Z^*_{air} - Z_{LIQ}^*).$$ (14)

The modulus of $Z_f^*$ can be determined from the slope of Eq. (13). The argument can be obtained from Eq. (14). Note that $2 \times \arg Z_f^* = \arg(G_f)$.

$Z_f^*$ can be obtained by direct measurement of the film in air and be replaced in Eqs. (13) and (14). However, this procedure occasionally yields bad correlated points for plots of these equations. We attribute this fact to the following factors: first, after the first addition of liquid, a very thin layer of poorly attached polymer can be stripped from the film, and, second, a tiny difference in temperature between air and solutions can change the viscoelastic properties of the film. It was found that simultaneous least square fits of $Z_f^*$ and $Z_f^*$ always gave good agreement with experimental values and excellent correlation with Eqs. (13) and (14). This approach also permits the measurement of rheological properties of films which must be kept in contact with a liquid layer to preserve their mechanical properties (highly solvated materials, hydrogels, etc.), since direct measurement of $Z_f^*$ in these materials is impossible.

Figure 8(a) shows the plots for the experimental data of the film in Fig. 7(c) (dots) compared with Eq. (13) (line). Parameters $Z_f^*$ and $Z_f^*$ were fitted using an iterative nonlinear least squares algorithm. Figure 8(b) shows Eq. (14) compared with the data for the film in Fig. 7(c).

$$\phi_f = \tan^{-1}(\alpha),$$ where $\alpha = G'/G''$ is the argument of $G$. Equation (14) predicts a zero slope for the plot, in excellent agreement with the experimental data. The other films yielded similar results. The fitted parameters $R_f^* = 80.9 \Omega$.

FIG. 7. Polar parametric plot of the data in Fig. 6. Dots: Experimental measurements for (a) the bare crystal and (b)–(d) the three films. Solid line: Evaluation of Eq. (10) for the bare crystal and the three films using the data in Tables I and II.
and \(X_{\text{air}}^\text{f} = 1484 \, \Omega\) were found to be close to the direct measurements, 60 and 1498 \(\Omega\). Table I shows the measured values for the three films.

Replacement of the measured parameters \(G'\) and \(G''\) in Eq. (4) and the nonlinear fit of parameter \(d\) gives a very accurate method to determine the thickness. The solid lines in Fig. 7 show a very good fit to the experimental data.

To determine the robustness of the method we derived the thickness \(d\) from Eqs. (1), (2), and (11).

\[
d = \frac{\pi \sqrt{\mu_0 \rho_0}}{2 \omega X_{\text{air}}^\text{f} \tan^{-1} \left( \frac{Z_{\text{air}}^\text{f}}{Z_{\text{f}}^\text{air}} \right)}.
\]

Despite Eq. (15) being in the complex plane, the magnitude for \(d\) must be real in order to represent a physical quantity.

Table II shows the values for \(d\) obtained for each film by replacing the fitted values \(Z_{\text{air}}^\text{f}\) and \(Z_{\text{f}}^\text{air}\) in Eq. (15). The imaginary part of \(d\) is much smaller than the real part, that is, the arguments of the vectors representing \(d\) are within 3° of the real axis. The real parts of \(d\) are within 5% of the values obtained by direct fitting of \(d\) using Eq. (4).

**CONCLUSIONS**

We have demonstrated that the mass and the rheological properties of thin films can be measured simultaneously using a quartz crystal resonator. The nonadditive acoustic impedance analysis permits the simultaneous determination of the film thickness \(d\), the storage modulus \(G'\), and the loss modulus \(G''\). We have also demonstrated that a very precise and independent determination of the thickness is a necessary condition for the application of standard impedance analysis, since bad estimations of thickness yield artifacts.

We applied a nonadditive impedance acoustic analysis to the measurement of viscoelastic properties of polystyrene-dioctylphthalate films. The experimental data were in excellent agreement with Martin’s model for nonpiezoelectric viscoelastic bilayers.

The method devised opens up the possibility of simultaneous determination of mass and rheological properties even for films that cannot be exposed to air. The method can be used simultaneously with photophysical or electrochemical techniques. Redox changes in the mechanical properties of hydrogel modified electrodes are being investigated using this approach.

**ACKNOWLEDGMENTS**

The authors give very special thanks to J. Olabe for fruitful and enriching discussions, and to L. Slep, V. Brudny, and C. D’Alessio for helpful assistance. This work was partially supported by Universidad De Buenos Aires (UBA) and Consejo Nacional De Investigaciones Científicas Técnicas (CONICET).

---

**TABLE II. Comparison of directly obtained thickness \(d\) calculated from Eq. (15) using \(Z_{\text{air}}^\text{f}\) and \(Z_{\text{f}}^\text{air}\) of the polystyrene-dioctylphthalate films in Figs. 7(b)–7(d).**

<table>
<thead>
<tr>
<th>(\text{Z}_{\text{air}}^\text{f}/\Omega)</th>
<th>(\text{Z}_{\text{f}}^\text{air}/\Omega)</th>
<th>Complex (d/\mu\text{m})</th>
<th>Fitted (d/\mu\text{m})</th>
</tr>
</thead>
<tbody>
<tr>
<td>69.1 + j860.7</td>
<td>2218.2 + j474.0</td>
<td>0.375 + j0.018</td>
<td>0.357</td>
</tr>
<tr>
<td>80.9 + j1484.2</td>
<td>2560.1 + j832.3</td>
<td>0.622 + j0.002</td>
<td>0.621</td>
</tr>
<tr>
<td>308.2 + j2231.7</td>
<td>2488.9 + j1301.1</td>
<td>0.918 + j0.022</td>
<td>0.939</td>
</tr>
</tbody>
</table>

---

32 R. Lucklum (private communication).