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Quantitative Measurements of Dielectric Spectra with Microdielectric Fringe-Effect Sensors

Yunn-Hong Choi and Mikhail Skliar*

Department of Chemical Engineering, University of Utah, Salt Lake City, Utah 84112

The parallel-plate method is a gold standard for measuring dielectric properties of materials. However, it requires sampling of the material under testing (MUT), which makes it less suitable for real time, dynamic, and in situ measurements. The alternative to the parallel-plate method is to use the microdielectric fringe-effect (FE) sensors, which can be placed inside the process or laboratory equipment to provide rapid, on-line, and noninvasive characterization of the dielectric properties. An additional potential advantage of the FE measurements is the ability to obtain spatially localized and interfacial measurements, which may be important in some applications. Unfortunately, interpretation of the FE sensor measurements is difficult because of the spatial nonuniformity of the electrical excitation field created by the FE sensor and the extraneous contributions from the sensor substrate and unknown stray elements. The objective of this study is to summarize the theoretical basis of the dielectric measurements using planar interdigitated sensors and to use it in the development of a new method for obtaining quantitative measurements with FE sensors. As the first step, the basic correlation between the impedance measurements obtained with the FE sensor and the dielectric properties of the MUT is elucidated. The theoretical results are then used to analyze the contribution of the sensor substrate and unknown stray components to the overall measurements. A novel calibration method to eliminate extraneous contributions is then proposed. The application example demonstrates the application of the developed method to the measurement of the dielectric permittivities of a polydispersed *cis*-polyisoprene samples. The results are compared with those obtained using the parallel-plate measurements and show excellent agreement. Experimental comparison with the alternative calibration methods is also performed, indicating significant improvement in accuracy of dielectric measurements over a broad range of frequencies.

Dielectric spectroscopy is a well-established method of material characterization, widely used in a variety of applications, including characterization of relaxation processes,^{1–3} phase transitions in

amorphous, crystalline, and liquid-crystalline polymers,^{4–6} and chain motion in rodlike polymers⁷ to mention just a few. The parallel-plate (PP) method is the standard approach to measure the dielectric properties: The material under testing (MUT) is placed between the parallel plates of a capacitor,⁸ and the excitation electrical field is applied to the plates. The interpretation of the measurements is straightforward due to the uniform intensity and direction of the probing field. The limitations of the standard approach in making dynamic and in situ measurements are related to the need to sample the MUT. Furthermore, the parallel-plate method is insensitive to the spatial inhomogeneity of the MUT and provides spatially averaged information on dielectric properties.

An alternative to the parallel-plate sensing is to probe the MUT using planar electrodes at the material interface, which create a fringing (or fringe-effect) electromagnetic field inside the sample. With use of microfabrication methods, the FE sensors can be miniaturized, making them sensitive to the dielectric properties in the immediate vicinity of the sensor–material interface. Furthermore, the miniature size and planar structure allows for the placement of the FE sensors inside the process and laboratory equipment for the dynamic and spatially localized measurements of the dielectric properties.

The FE sensors, originally developed by Senturia and co-workers,^{9,10} are typically comprised of a set of interdigitated electrodes microfabricated on an insulating substrate. The FE sensors have been used for a wide range of qualitative applications, such as humidity monitoring,^{11–13} the monitoring of the cure process,¹⁴ chemical detection,^{15–17} and biological material

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* To whom correspondence should be addressed. E-mail: mikhail.skliar@utah.edu. Fax: (801) 585-9291.

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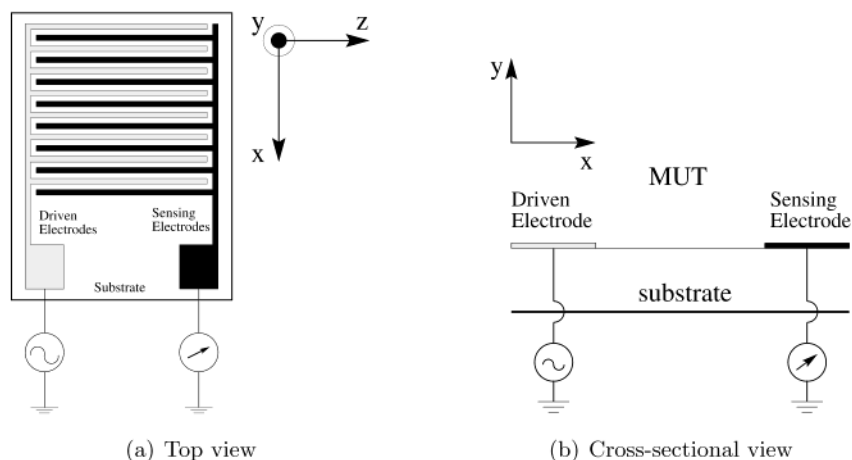


Figure 1. Schematic representation of a FE sensor: (a) Top view. The number of interdigitated electrodes is reduced for clarity. (b) Cross-sectional view in the x - y plane of a single electrode pair.

sensing.^{18–22} At the same time, the quantitative estimation of the dielectric properties using FE measurements proved to be difficult because of the following: (1) The contribution of the sensor's substrate to the overall measurements; (2) the effect of unknown stray elements related to the contact impedances between the sensor and the MUT, stray contributions associated with the connecting fixtures and leads, and the variability of the sensors introduced during the manufacturing; and (3) the standard calibration methods used with the parallel-plate sensors (such as load calibration with the known standard, short compensations, etc.) cannot be easily utilized with fringe-effect sensors.

The objective of the current work is to develop the methods for the quantitative measurements with fringe-effect sensors valid for the broad range of frequencies and materials under testing. After the theoretical results on the dielectric measurements with fringing field are summarized, the model relating the FE measurements to the dielectric properties of the sample is developed. The developed model is then used to analyze two existing calibration methods to explain why the calibration results are standard-dependent and applicable only in the limited range of frequencies. To account for the standard-dependent calibration of the FE sensor, a novel method is proposed, which only requires the parallel-plate dielectric measurements obtained for a sample known to be dielectrically similar to the unknown sample of the MUT. The application of the proposed method is illustrated by applying it to the FE dielectric measurements of the polydispersed *cis*-polyisoprene sample with the calibration obtained with the dissimilar polyisoprene sample. The dielectric spectra obtained with the proposed method is compared with the alternatives and the gold standard parallel-plate measurements. The results with

the proposed calibration method show excellent agreement with the results obtained using the parallel-plate method over the entire frequency range of the measurements.

FRINGE-EFFECT SENSOR

A fringe-effect sensor is the system of electrodes created on the substrate using microfabrication techniques. Figure 1 shows the schematic illustration of a typical FE sensor. The MUT sample is placed on the top of the electrodes, and the excitation voltage is applied to the sensor. The resulting excitation field is non-uniform and approximately two-dimensional. When the sinusoidal potential $\hat{q}_w = \varphi_d e^{j\omega t}$ is applied to the driven electrodes with the sensing electrodes grounded, the total charge on the sensing electrodes is expressed by the surface integral of the vector of complex electric field, $\hat{\mathbf{E}}(x, y, z, t) = \mathbf{E}(x, y, z) e^{j(\omega t + \phi)}$ over the surface of sensing electrodes, S ,

$$\hat{q} = \int_S \epsilon_0 \epsilon^* \hat{\mathbf{E}} \cdot d\mathbf{s} = \int_S \epsilon_0 \epsilon^* (\mathbf{E} e^{j(\omega t + \phi)}) \cdot d\mathbf{s} \quad (1)$$

where ϕ is a phase angle, \mathbf{s} is the unit normal vector in the outward direction perpendicular to the electrode surfaces, ϵ_0 is the dielectric constant of free space, ϵ^* is the relative dielectric permittivity of material surrounding electrodes and $\hat{\cdot}$ indicates complex quantity. The total electric current flowing into the sensing electrode can be expressed as

$$\hat{I} = \frac{d\hat{q}}{dt} = \omega \int_S \epsilon_0 \epsilon^* (\mathbf{E} e^{j(\omega t + \psi)}) \cdot d\mathbf{s} \quad (2)$$

where $\psi = (\phi + (\pi/2))$. If we express \hat{I} as a sum of currents through the sample, \hat{I}_a , and the substrate, \hat{I}_b , then

$$\hat{I} = [\omega \int_{S_a} \epsilon_0 \epsilon_a^* (\mathbf{E}_a e^{j(\omega t + \psi_a)}) \cdot d\mathbf{s}] + [\omega \int_{S_b} \epsilon_0 \epsilon_b^* (\mathbf{E}_b e^{j(\omega t + \psi_b)}) \cdot d\mathbf{s}] \quad (3)$$

where ϵ_a^* and ϵ_b^* are the dielectric permittivities of a sample and the substrate and S_a and S_b are parts of the electrode surface S in contact with the MUT and the substrate, respectively. The vectors

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of the electric field in the sample and substrate, \mathbf{E}_a and \mathbf{E}_b , are shifted by the phase angles ψ_a and ψ_b . The phases change with frequencies and the dielectric properties of the sample and substrate. With use of eq 3, the admittance of the FE sensor can be calculated as

$$\mathbf{Y}_{\text{sen}} = \frac{\hat{I}}{\hat{\varphi}_w} = \frac{\omega \epsilon_0}{\varphi_d} [\epsilon_a^* e^{j\psi_a} \int_{S_a} \mathbf{E}_a \cdot d\mathbf{s} + \epsilon_b^* e^{j\psi_b} \int_{S_b} \mathbf{E}_b \cdot d\mathbf{s}] \quad (4)$$

Consider an idealized case of FE sensor with vacuum substrate ($\epsilon_b^* = 1$) used to measure the vacuum "sample" (i.e., $\epsilon_a^* = 1$). For vacuum $R_v = \infty$, ψ_a and ψ_b are equal to $\pi/2$, and the sensor admittance in this case is equal to

$$\mathbf{Y}_v = j\omega \left[\frac{\int_{S_a} \epsilon_0 \mathbf{E}_a \cdot d\mathbf{s}}{\varphi_d} + \frac{\int_{S_b} \epsilon_0 \mathbf{E}_b \cdot d\mathbf{s}}{\varphi_d} \right] \quad (5)$$

Therefore, we can define the vacuum capacitance, C_v , of the FE sensor as

$$C_v = \frac{\int_{S_a} \epsilon_0 \mathbf{E}_a \cdot d\mathbf{s}}{\varphi_d} + \frac{\int_{S_b} \epsilon_0 \mathbf{E}_b \cdot d\mathbf{s}}{\varphi_d} \quad (6)$$

Vacuum capacitance C_v is independent of frequency and only depends on the design of the sensor. Thus, when the *geometric constant* k is introduced, two terms on the right-hand side of eq 6 can be expressed as

$$\frac{\int_{S_a} \epsilon_0 \mathbf{E}_a \cdot d\mathbf{s}}{\varphi_d} = kC_v \quad \frac{\int_{S_b} \epsilon_0 \mathbf{E}_b \cdot d\mathbf{s}}{\varphi_d} = (1 - k)C_v \quad 0 \leq k \leq 1 \quad (7)$$

With use of the introduced vacuum capacitance and the geometric constant, the admittance of the FE sensor is equal to

$$\begin{aligned} \mathbf{Y}_{\text{sen}} &= j\omega C_{\text{sen}} + \frac{1}{R_{\text{sen}}} \\ &= j\omega C_v \{ [\epsilon'_a \sin \psi_a - \epsilon''_a \cos \psi_a]k + \\ &\quad [\epsilon'_b \sin \psi_b - \epsilon''_b \cos \psi_b](1 - k) \} \\ &\quad + \omega C_v \{ [\epsilon'_a \cos \psi_a + \epsilon''_a \sin \psi_a]k + \\ &\quad [\epsilon'_b \cos \psi_b - \epsilon''_b \sin \psi_b](1 - k) \} \quad (8) \end{aligned}$$

obtained by taking into the account that $\epsilon_a^* e^{j\psi_a} = (\epsilon'_a - j\epsilon''_a) \cdot (\cos \psi_a + j \sin \psi_a)$ and the similar equality for $\epsilon_b^* e^{j\psi_b}$, where ϵ'_a and ϵ''_a are the dielectric storage and loss of the sample. The theoretical dependence of the resistance and capacitance of the FE sensor on the dielectric properties of the sample and the substrate, the sensor design, and the frequency of the probing electrical field is summarized by the following equations:

$$\begin{aligned} C_{\text{sen}} &= [\epsilon'_a \sin \psi_a - \epsilon''_a \cos \psi_a]kC_v + \\ &\quad [\epsilon'_b \sin \psi_b - \epsilon''_b \cos \psi_b](1 - k)C_v \quad (9) \end{aligned}$$

$$\begin{aligned} \frac{1}{R_{\text{sen}}} &= \omega [\epsilon'_a \cos \psi_a + \epsilon''_a \sin \psi_a]kC_v + \\ &\quad \omega [\epsilon'_b \cos \psi_b - \epsilon''_b \sin \psi_b](1 - k)C_v \quad (10) \end{aligned}$$

Equations 9 and 10 give the relationship between the impedance measurements of the FE sensor with the unknown MUT (typically obtained in the form of the resistance and capacitance spectra) and the dielectric properties of the sample $\epsilon_a^* = \epsilon'_a - j\epsilon''_a$. They indicate that, with the known dielectric properties of the sensor substrate, the calculation of (ϵ_a^*) from the measurements of $C_{\text{sen}}(\omega)$ and $R_{\text{sen}}(\omega)$ will require the knowledge of k , $\psi_a(\omega)$, and $\psi_b(\omega)$, where ψ_a and ψ_b generally depend on the dielectric properties of an unknown MUT sample.

Existing Methods. The calibration method developed in ref 23 and used in several studies (e.g., refs 3 and 24) is based on the hypothesis that the partitioning of the electrical field energy between the sample and the substrate is independent of frequency and the selected standard used to perform the sensor calibration. According to this method, the measured capacitance and resistance, C_m and R_m , are linear combinations of the dielectric storage and loss of the sample and the substrate. Therefore, calibration equations relating the measured resistance and capacitance spectra to the dielectric properties of the MUT are expressed as

$$C_m = k_f C_v \epsilon'_a + (1 - k_f) C_v \epsilon'_b \quad (11)$$

$$\frac{1}{R_m} = \omega k_f C_v \epsilon''_a + \omega (1 - k_f) C_v \epsilon''_b \quad (12)$$

where k_f is a constant independent of frequency and the sample. For the MUT with known dielectric properties, eq 11 defines a straight line with the slope $k_f C_v$, which can be determined using several standard samples. With use of the obtained $k_f C_v$, the dielectric storage and loss of an unknown sample can be calculated as

$$\epsilon'_a = \frac{C_m - C_0}{k_f C_v} + 1 \quad (13)$$

$$\epsilon''_a = \frac{1}{\omega k_f C_v} \left[\frac{1}{R_m} - \frac{1}{R_0} \right] \quad (14)$$

where C_0 and R_0 are the measured capacitance and resistance of air.

The comparison of eq 11 with the theoretical model (9) indicates that k_f is identical to the introduced geometric constant and that it is implicitly assumed that MUT and the substrate are zero-loss materials ($\psi_a = \psi_b = \pi/2$). However, the assumption of the zero loss current also implies that $R_m = \infty$ and $\epsilon''_a = \epsilon''_b = 0$, which, of course, is inconsistent with the calibration equation (12). Because the calibration equations (11) and (12) incorrectly capture the dependence of the measured C_m and R_m on the dielectric properties of a sample and substrate, ϵ_a^* and ϵ_b^* , we can expect

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substantial errors in estimating ϵ_a^* for different MUT samples, and as a function of frequency.

The calibration method suggested by the commercial supplier of the FE sensors (<http://www.micromet.com/>) is based on similar assumptions. According to the manufacturer's calibration method, the capacitance and resistance of the sensor are expressed as

$$C_m = \epsilon_0 k_m \epsilon'_a + C_{\text{base}} \quad (15)$$

$$\frac{1}{R_m} = \omega \epsilon_0 k_m \epsilon''_a + \frac{1}{R_{\text{base}}} \quad (16)$$

where, similarly to k_f of the first described method, k_m is the geometric constant of the sensor. The value of k_m is independent of frequency and the unknown sample, but changes with the sensor design, as specified by the manufacturer. For example, for MS-05 FE sensor used in the experimental study k_m is equal to 140. With use of N standard materials of known dielectric property, C_{base} and $1/R_{\text{base}}$ can be obtained as

$$C_{\text{base}} = \frac{1}{N} \sum_{i=1}^N (C_{m,i} - \epsilon_0 k_m \epsilon'_{a,i}) \quad (17)$$

$$\frac{1}{R_{\text{base}}} = \frac{1}{N} \sum_{i=1}^N \left(\frac{1}{R_{m,i}} - \omega \epsilon_0 k_m \epsilon''_{a,i} \right) \quad (18)$$

where $C_{m,i}$ and $R_{m,i}$ are the measured values obtained with the i th standard with known $\epsilon'_{a,i}$ and $\epsilon''_{a,i}$. The dielectric spectra of an unknown sample is then calculated as

$$\epsilon'_a = \frac{C_m - C_{\text{base}}}{\epsilon_0 k_m} \quad (19)$$

$$\epsilon''_a = \frac{1}{\omega \epsilon_0 k_m} \left[\frac{1}{R_m} - \frac{1}{R_{\text{base}}} \right] \quad (20)$$

The comparison of eqs 15 and 16 with the theoretical model reveals an implicit assumption of purely capacitive behavior of the sensor with the MUT. As with the first alternative, we can expect that the calibration method recommended by the manufacturer may cause significant errors in obtaining ϵ_a^* as a function of frequency, and with different unknown samples.

Proposed Method. The developed theoretical model, eqs 9 and 10, may be directly used to calibrate the FE sensors. However, for the FE sensor with a known substrate the determination of ϵ_a^* from (9) and (10) requires the knowledge of several calibration parameters, specifically k , ψ_a , and ψ_b . In this section we demonstrate that, under reasonable assumptions, the number of experimental calibration parameters required for obtaining quantitative dielectric measurements for the unknown sample may be reduced to a single frequency-dependent *partition function* $p(\omega)$.

1. Approximation of the FE Sensor Admittance. For low-loss dielectrics $\epsilon'' \ll \epsilon'$. Therefore, ψ_a and ψ_b can be approximated as $\psi_a \approx \psi_b \approx (\pi/2)$ but allow ψ_a to be a function of frequency:

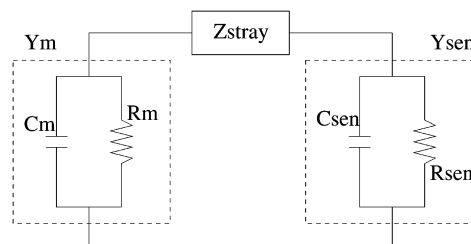


Figure 2. Corresponding equivalent circuit of a FE sensor for the proposed method.

$\psi_a = \psi_a(\omega)$. Then eqs 9 and 10 can be approximated as

$$C_{\text{sen}} = k \sin \psi_a C_v \epsilon'_a + (1 - k \sin \psi_a) C_v \epsilon'_b \quad (21)$$

$$\frac{1}{R_{\text{sen}}} = \omega k \sin \psi_a C_v \epsilon''_a + \omega (1 - k \sin \psi_a) C_v \epsilon''_b \quad (22)$$

where we used $\cos \psi_a \approx \cos \psi_b \approx 0$, $\sin \psi_b \approx \sin \psi_a$, and $(1 - k \sin \psi_a) \approx (1 - k \sin \psi_a)$. Introduction of the partition function $p(\omega) = k \sin \psi_a$ yields the proposed calibration equations

$$C_{\text{sen}} = p C_v \epsilon'_a + (1 - p) C_v \epsilon'_b \quad (23)$$

$$\frac{1}{R_{\text{sen}}} = \omega p C_v \epsilon''_a + \omega (1 - p) C_v \epsilon''_b \quad (24)$$

where $p(\omega)$ is a frequency-dependent function quantifying the partitioning of storage and dissipation of the electrical field in the substrate and the sample. Note that p depends on ψ_a and it therefore differs with the selection of the known samples used during the calibration. The sample dependency of the calibration is the limitation of all discussed calibration methods. The proposed method clarifies and makes explicit such a dependence. It also suggests that standard dependence of the results of the FE measurements can be mitigated by performing the calibration with the known materials dielectrically similar to the unknown MUT.

2. Series Stray Impedance. The calibration equations (23)–(24) are based on the theoretical model that does not account for the possible existence of the stray impedances introduced by the interconnecting leads, connection fixture, contact impedances, or FE sensor itself. With use of the series equivalent circuit of Figure 2 for the stray impedance, the relationship between the apparent (measured) impedance Z_m and the impedance of the FE sensor is given by the following equation:

$$Z_m = \frac{1}{Y_m} = Z_{\text{stray}} + \frac{1}{Y_{\text{sen}}} \quad (25)$$

where $Z_{\text{stray}} = R_{\text{stray}} + jX_{\text{stray}}$ and $Y_m = 1/R_m + j\omega C_m$. The contribution of Z_{stray} must be removed before performing calibration. The traditional compensation methods, such as short and load compensations utilized with parallel-plate sensor of identifying Z_{stray} , are based on the measurement of the impedance (e.g., $C_m(\omega)$ and $R_m(\omega)$ spectra) of known standard(s). The primary difficulty of applying the traditional method to the calibration of FE sensors is the variability introduced during the microfabrication of FE sensors and their connection to the measuring

instrument. Such variability affects the impedance measurements of standard materials. Consequently, each individual sensor must be calibrated without the benefit of knowing the “correct” impedance. To overcome this problem, we propose a calibration approach based on the known *dielectric spectra* of the standard materials. The dielectric properties are independent of unknown variabilities and can be easily obtained using the parallel-plate method. The calibration is then performed to match the permittivity calculated based on the FE sensor measurements to the known permittivity of the standard. The details of the combined calibration and compensation procedure are outlined below.

3. Estimation of the Dielectric Properties of the Sample.

Using the impedance measurements with two standard materials, we obtain

$$\mathbf{Z}_{m1} - \mathbf{Z}_{m2} = \left[\frac{R_{sen1}}{S_1} - \frac{R_{sen2}}{S_2} \right] - j\omega \left[\frac{C_{sen1}R_{sen1}^2}{S_1} - \frac{C_{sen2}R_{sen2}^2}{S_2} \right] \quad (26)$$

where $S_1 = 1 + \omega^2 C_{sen1}^2 R_{sen1}^2$ and $S_2 = 1 + \omega^2 C_{sen2}^2 R_{sen2}^2$, and the difference is independent of strays. The calibration equations (23) and (24) used in the above expression give

$$\mathbf{Z}_{m1} - \mathbf{Z}_{m2} = \left[\frac{p\epsilon'_1 + (1-p)\epsilon'_b}{\omega C_v D_1} - \frac{p\epsilon'_2 + (1-p)\epsilon'_b}{\omega C_v D_2} \right] - j \left[\frac{p\epsilon'_1 + (1-p)\epsilon'_b}{\omega C_v D_1} - \frac{p\epsilon'_2 + (1-p)\epsilon'_b}{\omega C_v D_2} \right] \quad (27)$$

where

$$D_1 = [p\epsilon'_1 + (1-p)\epsilon'_b]^2 + [p\epsilon'_1 + (1-p)\epsilon'_b]^2$$

$$D_2 = [p\epsilon'_2 + (1-p)\epsilon'_b]^2 + [p\epsilon'_2 + (1-p)\epsilon'_b]^2$$

The values of $p(\omega)$ and $C_v(\omega)$ can be found from the system formed by the real and imaginary parts of eq 27. With the known p and C_v , the stray impedance \mathbf{Z}_{stray} can be calculated using eq 25. The obtained p , C_v , and \mathbf{Z}_{stray} are saved and used in subsequent experiments to adjust C_m and R_m in order to remove the contribution of the strays and substrate before calculating the values of the dielectric storage and loss of an unknown sample. To derive the final expression for ϵ'_a and ϵ''_a , first note that after removal of the stray contribution,

$$\mathbf{Y}_{sen} = \left[\frac{1}{\mathbf{Y}_m} - \mathbf{Z}_{stray} \right]^{-1} \quad (28)$$

Thus, the compensated capacitance and resistance of the FE sensor is equal to

$$C_{sen} = \frac{M[\omega^2 C_m R_m^2 + \omega M X_{stray}]}{A} \quad (29)$$

$$\frac{1}{R_{sen}} = \frac{\omega^2 M[R_m - M R_{stray}]}{A} \quad (30)$$

where

$$M = 1 + \omega^2 C_m^2 R_m^2$$

$$A = \omega^2 [R_m - M R_{stray}]^2 + \omega^2 [\omega C_m R_m^2 + M X_{stray}]^2$$

With use of the calibration equations (23) and (24) the final expression for the dielectric spectra of an unknown MUT is calculated as

$$\epsilon'_a = \frac{M[\omega^2 C_m R_m^2 + \omega M X_{stray}]}{p C_v A} - \left(\frac{1-p}{p} \right) \epsilon'_b \quad (31)$$

$$\epsilon''_a = \frac{\omega M[R_m - M R_{stray}]}{p C_v A} - \left(\frac{1-p}{p} \right) \epsilon''_b \quad (32)$$

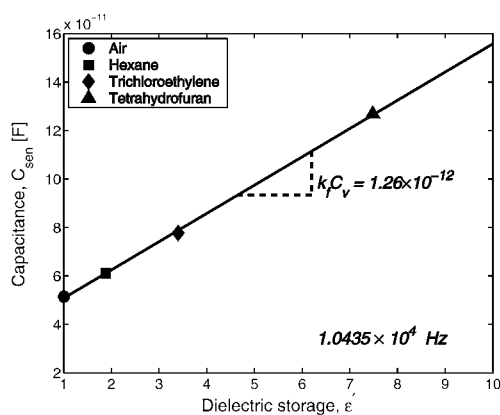
To achieve accurate results using the FE measurements, the standard materials used for sensor calibration should be dielectrically similar to the unknown sample. The sensor must be recalibrated (i.e., a new value of p must be found) each time the dielectric properties of unknown samples are changed significantly. In the example presented in the experimental part of the paper, the sensor calibration is done using one similar and one dissimilar sample. The polydispersed polymer sample with known dielectric spectra has the same chemical composition to the MUT, but differs in the average molecular weight and in the way it was synthesized. The second known sample is air and is dielectrically different from the MUT.

EXPERIMENTS

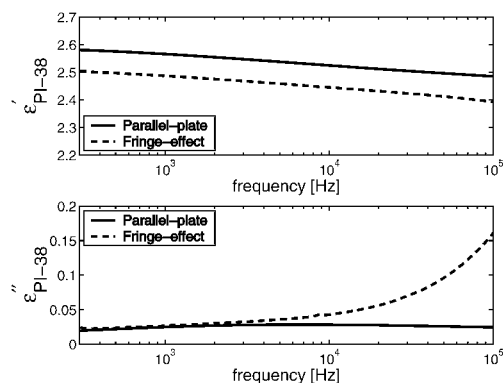
Materials. Two commercially available (Sigma-Aldrich) liquid *cis*-polyisoprene (*cis*-PI) samples were used in the present study. *cis*-PI has a permanent dipole moment parallel to the end-to-end vector of the main chain, which makes PI's normal mode dielectric spectra sensitive to the main-chain relaxation processes. Such polymers are traditionally classified as type-A polymers.²⁵ The dielectric relaxation in the lower frequency range of type-A polymers depends on the molecular weight distribution. The first polymer, PI-38, is a brown viscous liquid at room temperature with the average molecular weight of approximately 38 000 g/mol. PI-38 was obtained by depolymerization of natural rubber and was treated as an unknown sample during the experiments. The second *cis*-polyisoprene sample, PI-40, has an average molecular weight of 40 000 g/mol, appears as a viscous yellow liquid at room temperature and was obtained by depolymerization of synthetic *cis*-1,4-polyisoprene rubber. PI-40 was used as one of the standard materials during sensor calibration. Several nonconducting liquids (hexane, trichloroethylene, and tetrahydrofuran) were used for sensor calibration following the recommendations of the alternative calibration methods.

Dielectric Measurement. In the present study, the FE sensor with the 5- μ m spacing between the electrodes is used (MS-05, Micromet Instruments). The sensor consists of a periodic pattern of interdigitated chromium electrodes of equal width and spacing, microfabricated on a quartz substrate. The sensor has approximately 170 electrodes which are 5- μ m wide and 0.34-mm long.

(25) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539–554.



(a)



(b)

Figure 3. (a) Calibration curve for the FE sensor used to estimate $k_f C_v$. (b) The comparison of the dielectric spectra of PI-38, obtained using the first existing calibration method, with the results obtained using the PP method.

The parallel-plate measurements were carried out using a HP 16452A liquid test fixture. The impedance measurements, expressed in terms of $C_m(\omega)$ and $R_m(\omega)$ in the parallel equivalent circuit, are obtained using a HP 4284A precision LCR meter. In the experiments, the frequency sweep is applied to the PP fixture and the complex dielectric spectra is estimated using the standard equations for the PP sensor. The measurements are made at room temperature with the frequency sweep from 100 Hz to 1 MHz and 0.5-V testing potential. The PP measurements are compensated for sensor properties and stray elements using the short compensation method. The effect of the parasitic fringe fields on the edges of the PP sensor is compensated according to the manufacturer's recommendations.

The dielectric permittivity of the FE sensor substrate is measured by forming a parallel-plate capacitor using vacuum sputtering of the conductors on either sides of the dielectric substrate. The FE measurements of the MUT is carried out by placing a sample on top of the sensor connected to the HP4284A LCR meter using a custom-made connection fixture using a 4-terminal BNC connection method.

RESULTS AND DISCUSSION

Existing Methods. Figure 3a shows the measured C_m at 1.0435×10^4 Hz obtained with the FE sensor for air, hexane, trichloroethylene, and tetrahydrofuran as standards. The relative dielectric constants of these samples are known to be 1, 1.88, 3.4, and 7.48, respectively. The slope of the calibration line, equal to 1.126×10^{-11} F, is used as the estimation of $k_f C_v$. The dielectric spectra of an unknown sample is then estimated using eqs 13 and 14. The results for the PI-38 sample are shown in Figure 3b together with the results obtained using the gold-standard PP method. A substantial disagreement in the estimated value of the dielectric loss is apparent from the examination of the figure.

Figure 4 shows the results obtained following the manufacturer's recommendations. To stress standard dependence of the calibration, the results are presented for two calibration cases, obtained with different standards (air and hexane and air and PI-40). Comparison with the PP results indicate only slight improvement over the results presented in Figure 3b.

Proposed Method. With use of air and PI-40 as known samples, the calibration values of the partition function p and the

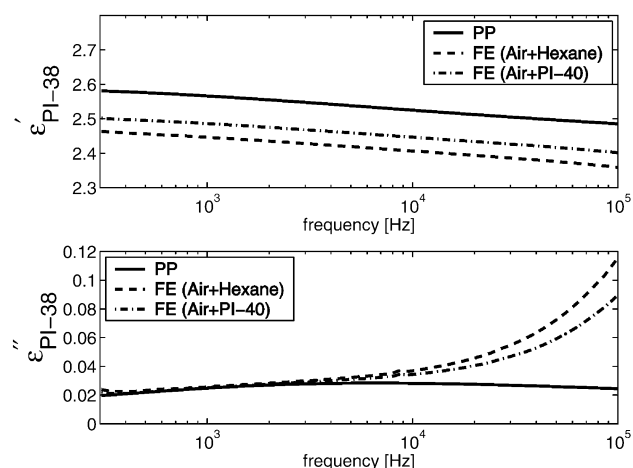


Figure 4. Comparison of the dielectric spectra of PI-38 obtained following manufacturer's recommendations, with the results obtained using the PP method.

vacuum capacitance C_v were found from the solution of eq 27 with the results shown in Figure 5a. Because of the approximations used to reduce the theoretical model (9)–(10) to the calibration equations (23)–(24), the estimated C_v is not a constant over all frequencies, as would be expected from the theory.

The stray impedance was calculated using eq 25, where \mathbf{Y}_{sen} was obtained using the calibration model (23)–(24). The values of the dielectric properties of the substrate were independently measured by forming the parallel-plate sensor using vacuum sputtering of the conductors on both sides of the sacrificed FE sensor, which has a substrate identical to that of the sensor used during FE measurements. The dielectric properties of the known sample (air in this case) were obtained using PP measurements.

Note that the described stray compensation method differs from the traditional load compensation since it is based on the known values of the dielectric spectra. Such modification was necessary since the impedance measurements with the known standard may actually vary from one FE sensor to another due to microfabrication variations and variability introduced during the establishment of the interconnections between the miniature sensor and the measuring instrument. Once the value of the $\mathbf{Z}_{\text{stray}}$ is established for a particular sensor, it is used in all subsequent

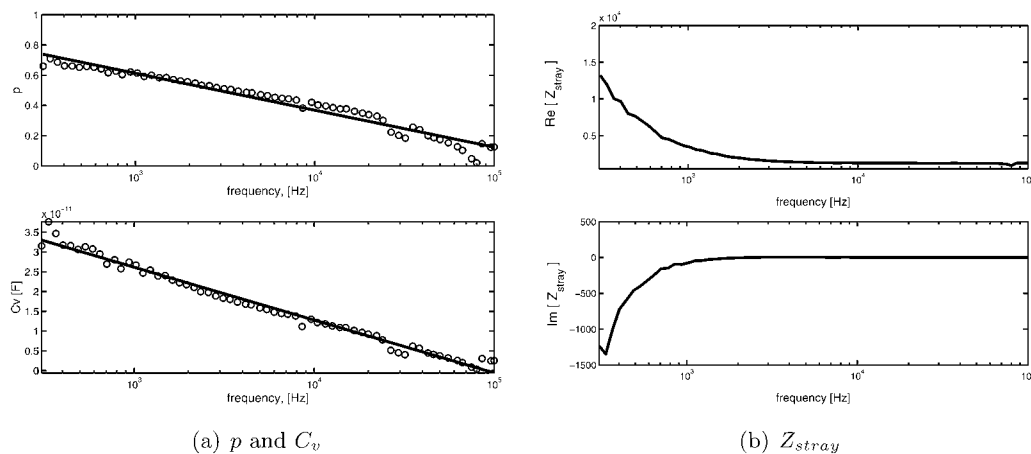


Figure 5. (a) The identified calibration of p , C_v . (b) The identified Z_{stray} .

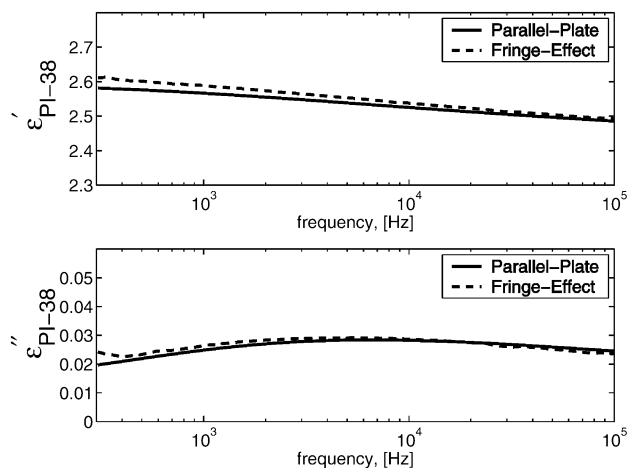


Figure 6. Comparison of the estimated dielectric permittivities of PI-38 obtained following the proposed method with the results based on PP measurements.

experiments to adjust the measured impedance to remove the contribution of the strays. The identified values of stray elements are plotted in Figure 5b.

The calibration results were then used to estimate the dielectric spectra of an unknown sample (PI-38) using eqs 31 and 32. The results are shown in Figure 6 and indicate close agreement with the dielectric spectra obtained using the PP method.

DISCUSSION AND CONCLUSIONS

Fringe-effect sensors have a potential for providing in situ, dynamic, and interfacial measurements of dielectric properties. However, obtaining the quantitative and reliable measurements with FE sensors is difficult. In this paper, we developed the theoretical model and proposed the experimental procedure for obtaining quantitative fringe-effect microdielectric measurements. The proposed method allows us to separate the contribution of the sensor substrate from the overall dielectric measurements. The sensor is characterized by the parallel connection of the admittance contributions from the substrate, Y_{sub} , and the sample, Y_{sam} : $Y_{sen} = Y_{sam} + Y_{sub}$. If Y_{sam} is known with two different samples, then Y_{sub} can be directly calculated from the impedance measurements. Unfortunately, even with the known samples, Y_{sam} is generally unknown because of variability of identically designed

sensors introduced during microfabrication, interconnection to the measuring instrument, and the variability in the way a sample is brought into contact with the sensor.

The proposed method performs the calibration based on the *dielectric spectra* of two samples, measured using the parallel-plate method. This removes the effect of unknown variabilities since the dielectric properties of the MUT remain constant. The calibration is designed to estimate the contribution of substrate and stray elements such that the dielectric spectra of the standard, calculated based on FE measurements according to eqs 31 and 32, match the results obtained with gold standard parallel-plate measurements. The proposed method performs calibration by matching dielectric permittivities of the known standard, as opposed to matching standard impedance measurements, as done during the traditional load compensation.

The results of the calibration are dependent on standards. To achieve highly accurate dielectric measurements, it is advisable to perform the calibration with the standard materials dielectrically similar to an unknown sample. This restriction is mitigated by the fact that the proposed calibration method is based on the dielectric spectra easily obtainable using the parallel-plate method. Since we can often anticipate the type of unknown samples that we will encounter in the future, the calibration can be performed with the dielectrically similar material, characterized using the standard PP techniques. The proposed method for quantitative fringe-effect measurements includes the procedure for the compensation of unknown stray contributions, which should be performed once for every sensor put into service.

The experimental study with polydispersed polymer samples was used to illustrate the application of the proposed method. It demonstrated high achievable accuracy with the proposed method in measuring dielectric spectra over the broad range of excitation frequencies.

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