Broadband Dielectric Metrology for Polymer Composite Films

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Abstract: We evaluated the dielectric permittivity and relaxation in polymer composite films filled with ferroelectric ceramics. Such materials are currently being developed for power-ground decoupling in electronic circuits operating at microwave frequencies. In order to extend the measurements to the microwave range, we developed an appropriate expression for the input admittance of a thin film capacitance terminating a coaxial line. The theoretical model treats the capacitance as a distributed network and correlates the network scattering parameter with complex permittivity of the specimen. The method eliminates the systematic uncertainties of the lumped element approximations and is suitable for high frequency characterization of low impedance substrates with high value of the dielectric constant. The complex permittivity was measured at frequencies of 100 Hz to 10 GHz for films 100 μm thick, having the dielectric constant of 4 to 40, and was fitted to a dielectric model expressed as a combination of Havriliak-Negami functions. An intrinsic high frequency relaxation process has been identified. It was found that the position of the loss peak depends on the relaxation of polymer matrix, while its magnitude is amplified by the permittivity of the ferroelectric component.

Introduction

To advance miniaturization and improve functional performance of high-speed electronics, there is growing need for dielectric films with high permittivity. Such materials can be used to construct integrated passive devices embedded within chip substrates and printed circuit sub-assemblies. Recently, high dielectric constant polymer-ferroelectric ceramic composites have shown promise for embedded de-coupling capacitance and power planes with desirable, low impedance characteristics over a broad frequency range, including the microwave [1]. However, the dielectric relaxation behavior and the origin of the high frequency dispersion in polymer-ceramic composites is still poorly understood [2] and typically attributed to the domain structure of the ceramic component [3].

In this paper we discuss the high frequency relaxation behavior in model polymer composites filled with ferroelectric barium titanate powder. The complex permittivity was measured in the frequency range of 100 Hz to 10 GHz. At frequencies above 100 MHz we used a coaxial test fixture [4]. The method eliminates the systematic uncertainties of the lumped element approximation, and allows accurate measurements at higher frequencies including the microwave range. We analyze the high frequency relaxation process in the polymer matrix and composites by fitting the experimental complex permittivity to a dielectric model expressed with the Havriliak-Negami functions.

Experimental Procedure

Materials: Trimethylolpropane triacrylate (TMPTA), and poly(ethylene glycol) diacrylate (PEGDA) were obtained from Aldrich. Barium titanate powder $(BaTiO_3)$ with an average particle size of about 0.3 μm to 3 μm was obtained from Aldrich and used as the ferroelectric filler. Prior to use $BaTiO_3$ was dried at 80 °C under vacuum for 24 hours. All materials, film preparation and curing procedures were handled in a dry box under argon atmosphere. Liquid mixtures were prepared by dispersing appropriate proportions of $BaTiO_3$ powder with the monomers. The composites were cured between glass slides at 80 °C for 16 hours in the presence of 0.1 % benzoylperoxide. The resulting films were typically 95 μm to 100 μm thick with the thickness spatial distribution of about 1 %. Circular, 3 mm diameter aluminum electrodes were deposited on both sides under vacuum through a mask.

Dielectric measurements: Figure 1 shows a diagram of the coaxial test fixture where a disk specimen of thickness d and the relative complex permittivity
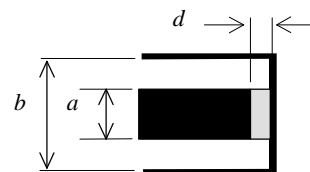

Figure 1 Diagram of the test fixture

$e^* = e' - je''$ is placed at the end of the center

conductor of a coaxial airline. The diameter of the specimen, a, matches that of the center conductor. Such structure has been assumed to satisfy the lumped capacitance approximation if the length of the propagating wave is much larger than the film thickness. In our previous [4] work we showed however, that the configuration depicted in Figure 1 is electrically equivalent to a network, where the dielectric film represents a transmission line inserted between two matched transmission lines. If $d << a$, then the primary propagation mode satisfying the boundary conditions in the specimen section is associated with the diameter of the film specimen rather than its thickness. The input admittance, Y_{in} given by (1), includes the combination of the wave multiple reflection and transmission components in the specimen section.

$$Y_{in} = G_s \frac{(1-r)(1-e^{-ga})}{(1+r)(1+e^{-ga})} \quad (1)$$

where: G_s is characteristic conductance of the specimen, ρ is the complex reflection coefficient for non-magnetic media; $r = (1-\sqrt{e*})/(1+\sqrt{e*})$; γ is the propagation constant, $g = jw/c\sqrt{e*}$; w is an angular frequency; and c is the speed of light in air. Introducing $x = \frac{wa}{2c}\sqrt{e*}$, (1) can be expressed as:

$$Y_{in} = G_s \frac{jwa}{2c} e* \frac{1}{x\cot(x)} \quad (2)$$

During measurements, the reference plane is set at the interface between the end of the coaxial line having the characteristic conductance, G_l, and the dielectric specimen section with the characteristic conductance G_s. A cell constant parameter, G_s/G_l, can be determined by evaluating the fringing field capacitance, C_f, around the specimen section [5]. Using the fringing field capacitance and (2), we finally arrive at (3) for the complex permittivity of the film specimen:

$$e* = \frac{G_l}{jwC_p} \frac{1-S_{11}^m}{1+S_{11}^m} \cdot x\cot(x) - \frac{C_f}{C_p} \quad (3)$$

where S_{11}^m is the measured scattering coefficient of the network. The value of the C_f/C_p ratio decreases to zero with decreasing film thickness. At sufficiently low frequencies, $x\cot(x)$ approaches value of 1.0

and (3) simplifies to the conventional lumped element model [3], which can be used for initial guessing in iterative solution of (3).

Measurements: A coaxial test fixture was constructed from two APC−7 mm to APC−3.5 mm microwave adapters [4]. The measurements were carried out using a network analyzer (HP 8720D). One-port open, short and broadband load calibration was performed using a HP 85050B APC-7 calibration kit. The relative combined standard uncertainty in geometrical capacitance measurements was typically 2 % with the primary contribution from the uncertainty in the film thickness measurements. The relative standard uncertainty of S_{11}^m was assumed to be within the manufacturer's specification for the HP 8720D. The combined relative experimental uncertainty in complex permittivity was within 8 % while the experimental resolution of the dielectric loss tangent measurements was about 0.01.

Results and discussion

The dielectric constant ε' and the dielectric loss factor ε'' increase in both composites with increasing concentration of BaTiO$_3$. Figure 2 illustrates the dependence of the dielectric constant of the TMPTA/BaTiO$_3$ and the PEGDA/BaTiO$_3$ composites on volume fraction φ of the barium titanate filler. The polymer matrices have each distinguishable dielectric properties to diversify the electromagnetic responsiveness of the corresponding composites. The dielectric constant of TMPTA polymer in the low frequency range is lower than the dielectric constant of PEGDA due to lower polarizability and lower concentration of molecular dipoles in TMPTA. For
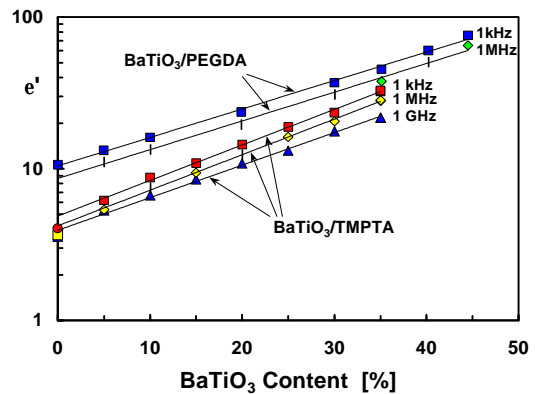

Figure 2. Dependence of the dielectric constant on the volume fraction of BATiO$_3$ at selected frequencies for TMPTA and PEGDA.

example, at 1 MHz the ε' of neat TMPTA polymer is 3.7 while the corresponding value of ε' for PEGDA polymer is about 10. Consequently, the dielectric constant of the TMPTA composites is lower than the dielectric constant of the corresponding PEGDA composites. The relationship between the dielectric constant of the composite and the volume fraction of the filler follows the logarithmic mixing rule, as expected for pure two component mixtures.

The broadband experimental permittivity data indicate that both composites exhibit considerable dielectric dispersion, which gives rise to the frequency dependent dielectric loss.

In order to analyze the dispersion behavior in more detail, we fitted the experimental complex permittivities to a general dielectric model (4), which is a superposition of Havriliak-Negami functions [6]:

$$e*(w) = e_\infty + \sum_{i=1}^{N} \frac{\Delta e_i}{(1 + (jwt_{0i})^{b_i})^{a_i}} \quad (4)$$

where e is the high frequency limiting permittivity and N represents the number of relaxation processes. For the i-th relaxation process going from the lower frequency side, $\Delta\varepsilon_i$ is the relaxation strength, τ_{0i} the relaxation time, α_i and β_i are the parameters representing asymmetric and symmetric distributions of relaxation time, respectively. The positive parameters α_i and β_i must satisfy the condition $0 < \alpha_i \beta_I <= 1$. The case of $\alpha_i = \beta_i = 1$ corresponds to the Debye type relaxation. The relaxation process corresponds to the Cole-Cole type when $\alpha_i = 1$ and $0 < \beta_i < 1$, and Davidson-Cole type when $0 < \alpha_i < 1$ and $\beta_i = 1$.

For the TMPTA composites, the frequency dependent complex permittivity can be described by four relaxation processes, three are corresponding to relaxation of the polymer matrix and one to the relaxation in BaTiO$_3$. This process has the relaxation frequency of about 10 GHz, which is consistent with the frequency behavior of the complex permittivity of the ceramic barium titanate observed by Poplavko [7]. Two molecular relaxations of the polymer backbone, and one additional process that corresponds to the relaxation in BaTiO$_3$ can describe the complex permittivity of PEGDA composites. Figures 3 and 4 illustrate that the fitting results agree well with the experimental data. The position of the high frequency loss peak of the TPMTA polymer is at about 30 MHz (Figure 3). It is seen that the magnitude of the loss peak increases with increasing volume fraction of the BaTiO$_3$ while the peak position remains essentially unchanged. In

comparison, the relaxation frequency of the fastest relaxation process in PEGDA is about 200 MHz (Figure 4), about an order of magnitude higher than the corresponding relaxation in TMPTA, which
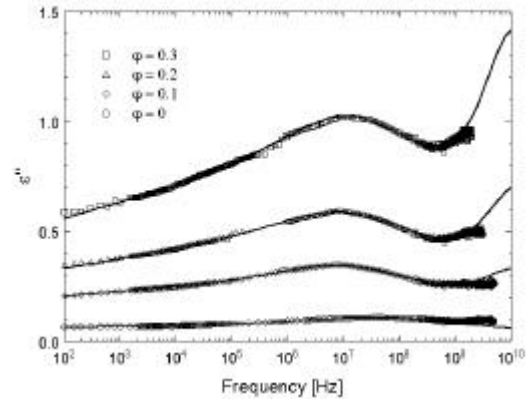

Figure 3. Dielectric loss of TMPTA and composites for several BaTiO$_3$ volume fractions φ (points) compared with the calculated results (solid lines).

results from structural differences of the polymer matrix. Nevertheless, the dielectric loss of the PEGDA/BaTiO$_3$ composite increases with increasing BaTiO$_3$ content without any significant change in the relaxation frequency similarly to that seen in the TMPTA/ BaTiO$_3$ composites.
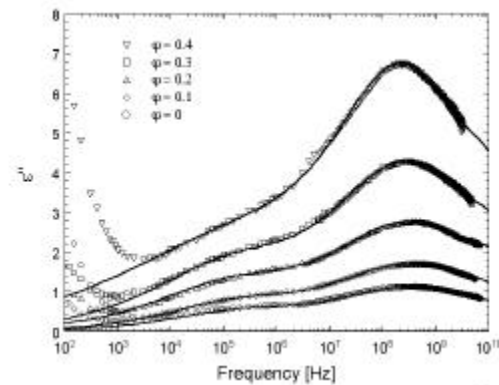

Figure 4. Dielectric loss of PEGDA and composites for several BaTiO$_3$ volume fractions φ (points) compared with the calculated results (solid lines).

The values of fitting parameters, where the uncertainties were estimated as 95 % confidence limit in χ^2 distribution, clearly indicate that the composites exhibit multiple relaxations due to molecular dynamics of the polymer matrix. For both polymer-ceramic composites, De increases with increasing j. Since the integrated loss is directly proportional to De, the dielectric dispersion is amplified by the volume fraction of the ferroelectric component. Consequently, the magnitude of the dielectric loss

increases with increasing j proportionally to increasing De. On the other hand, to within fitting uncertainty, the relaxation time is approximately independent on the content of the ceramic component. The experimental results show that the character of the dielectric loss spectra does not change with increasing fraction of $BaTiO_3$. The parameters α and b were found nearly independent on j for both composites, which indicates that the distribution of the relaxation time of the polymer matrix remains essentially unchanged by the ferroelectric component. Thus, the position of the loss peak is determined primarily by relaxation of the polymer matrix. Polymer matrix with shorter relaxation time, such as PEGDA, shifts the loss peak position to higher frequencies, while higher polarizability can increase magnitude of the dielectric loss. Thus, both the value of the dielectric constant as well as the position and magnitude of the loss peak can be quantitatively controlled by modifying the composition of the dielectric material at the molecular level.

Conclusion

The presented broadband measurement methodology that we developed for dielectric films eliminates systematic uncertainties of the conventional lumped element approximations and enables accurate evaluation of permittivity at frequencies of practical importance, above 1 GHz. Using this technique, we discovered that the composites of organic polymer resins with ferroelectric ceramics exhibit an intrinsic high frequency relaxation behavior. The position of the dielectric loss peak is controlled by the dielectric relaxation of the polymer matrix while the content and permittivity of the ceramic component amplify its magnitude. Furthermore, for each relaxation process the dielectric loss is quantitatively related with the dielectric increment of that process. The magnitude and position of the dielectric loss peak can be tailored by modifying the molecular structure of the polymer matrix. This makes polymer composites films very attractive as a broadband embedded de-coupling in electronic circuits operating at microwave frequencies.

Acknowledgment

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