High frequency dielectric relaxation in polymers filled with ferroelectric ceramics

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ABSTRACT

We investigated the dielectric relaxation process in high-dielectric constant polymer composite films filled with barium titanate particles. In order to extend the dielectric measurements to the microwave range, we employed a new broadband measurement technique where a thin film capacitance terminating a coaxial waveguide is treated as a transmission line. The complex permittivity, measured at frequencies of 100 Hz to 10 GHz for several films 50 μm to 100 μm thick with a dielectric constant of 3.2 to 30, was fitted to a dielectric model expressed as a superposition of Havriliak-Negami functions. An intrinsic high frequency relaxation process has been identified. It was found that the position of the loss peak depends primarily on the relaxation of the polymer matrix, while its magnitude is amplified by the volume fraction and permittivity of the ferroelectric component.

INTRODUCTION

Dielectric films with high permittivity can be used to construct advanced integrated passive devices such as capacitors and de-coupling power planes, which can be embedded within chip substrates and printed circuit sub-assemblies. Recently, high dielectric constant polymer-ferroelectric ceramic composites have been shown to have desirable electromagnetic characteristics over a broad frequency range, including the microwave[1]. Miniaturization of wireless sensing implants requires flexible films with appropriate dielectric properties [2]. Broadband permittivity is a key parameter needed to assess the role of materials microstructure on the polarization dynamics. In this paper we discuss the local, fast relaxation properties of polymer - ferroelectric ceramics composites. The relaxation process was analyzed by fitting the experimental complex permittivity in a broad frequency range of 100 Hz to 10 GHz to a dielectric model expressed as combination of Havriliak-Negami functions.

EXPERIMENTAL

Materials

We selected two acrylate monomers, trimethylolpropane triacrylate (TMPTA) and poly(ethyleneglycol) diacrylate (PEGDA), as representative models of crosslinked and linear polymer networks, respectively. The monomers were obtained from Aldrich[1] and used without

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[1] Certain materials and equipment identified in this manuscript are solely for specifying the experimental procedures and do not imply endorsement by NIST or that they are necessarily the best for these purposes.

further purification. Barium titanate powder ($BaTiO_3$ or BT), with an average particle size of about 0.3 μm to 3.0 μm, was obtained from Aldrich and used as the high dielectric constant filler. Prior to use, $BaTiO_3$ was dried at 80 °C under vacuum for 24 h. Liquid mixtures were prepared by dispersing appropriate proportions of $BaTiO_3$ powder in the monomers. Compositions were homogenized in an ultrasound stirrer and then cured between optical quality quartz slides into 100 μm thick films as described earlier [3]. Materials, film preparation and curing procedures were handled under an argon atmosphere.

Measurements

Measurements of the dielectric permittivity in the low frequency range of 100 Hz to 10 MHz were carried out in accordance with the ASTM D150 standard test method [4], using an Agilent 4294A Precision Impedance Analyzer. In the frequency range of 1 MHz to 400 MHz, we utilized a HP 4191A RF Impedance Analyzer and calculated the complex permittivity from reflection measurements on 3.0 mm diameter film specimens [5].

The complex permittivity in the microwave range was determined using a new broadband testing technique where a thin film capacitance terminating a coaxial waveguide is treated as transmission line. The theoretical model treats the capacitance as a distributed network and correlates the network scattering parameter with complex permittivity of the specimen. This method eliminates the systematic uncertainties of the lumped element approximation, which fail to produce meaningful results at frequencies above a few hundred megahertz [6,7]. Measurements of the scattering parameter S_{11}^m at frequencies of 100 MHz to 12 GHz were carried out using a network analyzer (Agilent 8720D) and a coaxial test fixture where a 3.0 mm diameter film specimen short-terminated an APC-7 coaxial transmission line. One-port open, short and broadband load calibration was performed using a HP 85050B APC-7 calibration kit.

Data obtained from different instruments were combined together into a single broadband dielectric spectrum. The relative combined standard uncertainty in geometrical capacitance measurements was 1 %. The largest contributing factor to the uncertainty was the uncertainty in the film thickness measurements of 1 μm. The relative standard uncertainty of S_{11}^m was assumed to be within the manufacturer's specification for the Agilent 8720D. The combined relative experimental uncertainty in complex permittivity was within 8 % while the experimental resolution of the dielectric loss tangent measurements was approximately 0.01.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the dielectric constant ε' and the dielectric loss ε'' on frequency for TMPTA-BT composites at room temperature for several concentrations of BT filler. Figure 2 shows analogous results obtained for PEGDA-BT composites.

The dielectric constant of the TMPTA polymer is lower than the dielectric constant of PEGDA due to the lower polarizability and concentration of molecular dipoles in TMPTA. For example, at 1 MHz, the ε' of neat TMPTA polymer is 3.7 while the corresponding value of ε' for the PEGDA polymer is about 10. Both polymers show a frequency dependent dispersion of ε', indicating a complex relaxation behavior. In the frequency range of 1 MHz to 1 GHz, ε' of
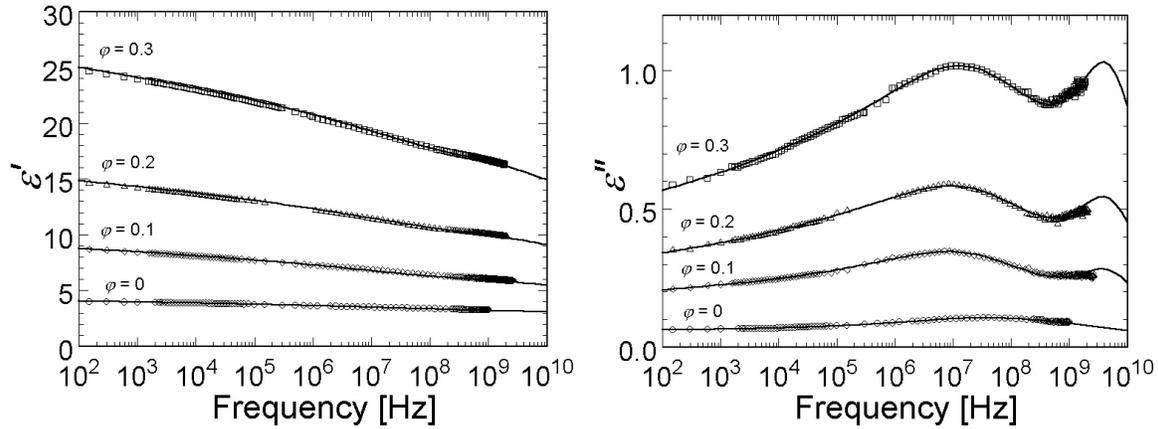
Figure 1. Dielectric constant ε' and dielectric loss ε'' of TMPTA polymer composite films for various volume fraction φ of barium titanate. Solid lines represent the fitting results.

TMPTA decreases by about 0.6 while in case of PEGDA polymer, ε' decreases by about 4.1. Since PEGDA exhibits a broader dispersion than TMPTA, the dielectric loss of PEGDA increases with frequency considerably more than that of TMPTA. A dominant peak in the dielectric loss, ε'', can be seen around 30 MHz for TMPTA (Figure1) and around 200 MHz for PEGDA (Figure 2).

In comparison to the pure polymers, the dielectric constant ε' of the corresponding composites increases with increasing volume fraction φ of BaTiO$_3$ (Fig. 1 and 2) where the relationship between ε' and φ appears to follows a logarithmic law [3]. For example, at 1 GHz, ε' of TMPTA increases from 3.2 ($\varphi = 0$) to 16.7 ($\varphi = 0.3$). In the case of the PEGDA composites, the dielectric constant is higher than that of the TMPTA composites at the corresponding volume fraction and it increases from 5.1 ($\varphi = 0$) to about 19.5 ($\varphi = 0.3$). In contrast, the dielectric loss behaves in a more complicated fashion. It appears that the dielectric loss ε'' of the composites evolves as a magnified dielectric loss spectrum of the polymer matrix where the increase in magnitude correlates with the amount of the ceramic component.

In order to analyze the relaxation behavior in more quantitative detail, we fitted the
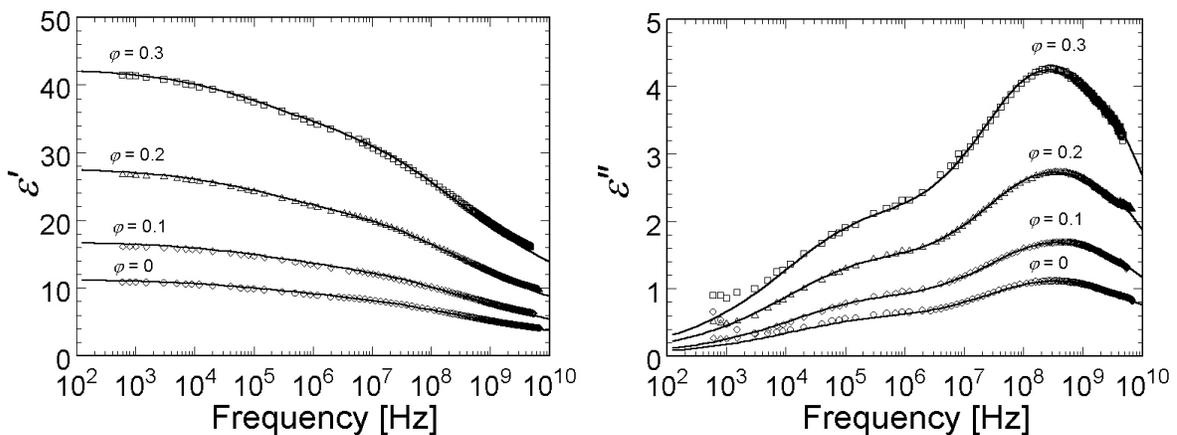
Figure 2. Dielectric constant ε' and dielectric loss ε'' of PEGDA polymer composite films for various volume fraction φ of barium titanate. Solid lines represent the fitting results.

experimental complex permittivities $\varepsilon^*(\omega)$ to a dielectric model (1), which is a superposition of Havriliak-Negami functions [8].

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_{i=1}^{N} \frac{\Delta\varepsilon_i}{\left\{1 + (j\omega\tau_{0i})^{\beta_i}\right\}^{\alpha_i}} \tag{1}$$

In (1) ω is the angular frequency, ε_∞ the high frequency limiting permittivity and N the number of the relaxation processes. For the i-th relaxation process, going from the lower frequency side, $\Delta\varepsilon_i$ denotes the relaxation strength, τ_{0i} is the relaxation time while 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 a condition $0 < \alpha_i\beta_i \le 1$. Since (1) can simplify to the Debye relaxation model ($\alpha_i = \beta_i = 1$), the Cole-Cole model ($\alpha_i = 1$, $\beta_i \ne 1$) or the Davidson-Cole model ($\alpha_i \ne 1$, $\beta_i = 1$), it is very useful in analyzing complex dielectric systems such as polymer-ceramic composites. The values of $\Delta\varepsilon_i$, τ_{0i}, α_i and β_i were determined by fitting equation (1) to the experimental data. The fitting procedure was guided by using the following residual function:

$$F_r = \frac{1}{m}\sqrt{\sum_{k=1}^{m}(\delta\varepsilon(\omega_k))^2} \tag{2}$$

where m is the number of data points, $\delta\varepsilon(\omega)$ is the residual. The fitting parameters were adjusted until the real (ε') and imaginary (ε'') parts of the residual functions simultaneously reached small values. The F_r value for ε', ($F_r(\varepsilon')$), was approximately 1 % of ε' measured at a low frequency plateau (1 kHz) in all samples. $F_r(\varepsilon'')$ was less than 5 % of the experimental dielectric loss maximum (ε''_{max}) in TMPTA, while it was about 1 % of ε''_{max} in the case of PEGDA composites, except in the case of pure PEGDA for which $F_r(\varepsilon'')$ was approximately 12 % of ε''_{max}. Since the F_r function indicates an average of residual for each data point, the calculated results are considered to give a significant fit, with respect to the combined relative uncertainty of 3 % for ε' and 5 % for ε''. The fitting results are illustrated as solid lines in Fig. 1 and 2, where they compare well with the experimental permittivities. Low frequency dielectric measurements conducted at temperatures of –150 °C to + 120 °C revealed that above 100 Hz the TMPTA polymer exhibits three distinguishable relaxation processes while the PEGDA polymer shows two relaxations. Therefore, we fitted the room temperature frequency dependent complex permittivity of TMPTA to three relaxation processes. Similarly, we assumed two relaxations in the case of complex permittivity spectra of PEGDA. In the composites ($\varphi > 0$), in addition to the polymer relaxations, there is an additional relaxation process associated with the loss maximum at about 5 GHz arising from the presence of barium titanate filler. The dielectric relaxation parameters for the highest frequency process in polymer matrix and that for the filler are listed in Tables 1 and 2.

The dielectric loss peak position of the barium titanate filler is found close to 5 GHz in both TMPTA ($f_{0\,4}$) and PEGDA ($f_{0\,3}$) polymer composites, which agrees well with the earlier results on the dielectric spectroscopic behavior of BaTiO$_3$ ceramics [9].

Table 1. Parameters of the high frequency relaxation for TMPTA-BT composites at various volume fractions φ of BaTiO$_3$. The frequency, f_0, and ε'' at f_0 are also shown.

φ	$\Delta\varepsilon_\infty$	$\Delta\varepsilon_3$	$\log \tau_{03}$	α_3	β_3	f_{03} (Hz)	$\varepsilon''(f_{03})$
0	2.889	0.691	-8.020	0.454	0.411	$1.667\ 10^7$	0.075
0.1	5.227	1.506	-8.004	0.874	0.411	$1.606\ 10^7$	0.240
0.2	8.541	2.697	-8.004	0.795	0.402	$1.606\ 10^7$	0.402
0.3	13.758	5.163	-8.007	0.715	0.397	$1.617\ 10^7$	0.720
φ		$\Delta\varepsilon_4$	$\log \tau_{04}$	α_4	β_4	f_{04} (Hz)	$\varepsilon''(f_{04})$
0.1		0.384	-10.506	1.000	0.901	$5.103\ 10^9$	0.164
0.2		0.734	-10.498	1.000	0.901	$5.010\ 10^9$	0.314
0.3		1.333	-10.509	1.000	0.901	$5.138\ 10^9$	0.570

Table 2. Parameters of the high frequency relaxation for PEGDA-BT composites at various volume fractions φ of BaTiO$_3$. The frequency, f_0, and ε'' at f_0 are also shown.

φ	$\Delta\varepsilon_\infty$	$\Delta\varepsilon_2$	$\log \tau_{02}$	α_2	β_2	f_{02} (Hz)	$\varepsilon''(f_{02})$
0	1.985	6.820	-9.141	0.742	0.422	$2.202\ 10^8$	1.035
0.1	3.162	9.572	-9.144	0.769	0.439	$2.217\ 10^8$	1.542
0.2	5.798	14.460	-9.146	0.848	0.445	$2.228\ 10^8$	2.476
0.3	10.384	20.733	-9.147	0.939	0.464	$2.233\ 10^8$	3.868
φ		$\Delta\varepsilon_3$	$\log \tau_{03}$	α_3	β_3	f_{03} (Hz)	$\varepsilon''(f_{03})$
0.1		0.304	-10.508	1.000	0.901	$5.126\ 10^9$	0.130
0.2		0.937	-10.508	1.000	0.901	$5.126\ 10^9$	0.401
0.3		1.801	-10.503	1.000	0.901	$5.068\ 10^9$	0.770

Perhaps the most interesting is the high frequency relaxation process that extends into the microwave frequency range. According to the fitting results, the highest relaxation frequency is about 16 MHz in TMPTA (Table 1, f_{03}) and about 220 MHz in PEGDA (Table 2, f_{02}). Thus changing the polymer matrix from a 3 dimensionally crosslinked polymer with a high Tg (TMPTA) to a linear polymer with a low Tg (PEGDA) shifts the highest frequency local relaxation from 16 MHz to about 220 MHz. On the other hand, it is seen that the relaxation time (τ_{03} for TMPTA and τ_{02} for PEGDA) does not change significantly with increasing volume fraction φ of BaTiO$_3$. However, the distribution of the relaxation time appears affected by the BaTiO$_3$ filler. In particular, the parameter α_3 (TMPTA) and α_2 (PEGDA), which represent asymmetric dispersion of the relaxation times, changes with increasing φ. The high frequency local relaxation process is more complex than it could be described by simple Cole-Cole or Davisdon-Cole models. The data indicate that the magnitude of the dielectric loss in composites increases with increasing volume fraction of φ. This effect is largest for the highest frequency relaxations, τ_{03} (TMPTA) and τ_{02} (PEGDA). Data shown in Tab. 1 and 2 indicate that the magnification of the loss peak seen in the presence of barium titanate filler is due to the increasing strength of dielectric dispersion $\Delta\varepsilon_i$ of i-th relaxation process that itself originates

from the polymer matrix relaxation. An increase in $\Delta\varepsilon_i$ is caused by the dielectric properties of barium titanate filler, which has a high dielectric constant. It can be noted that with increasing volume fraction, the loss peak around 5 GHz, identified in $BaTiO_3$ also increases. However, it only marginally contributes to the highest frequency dielectric loss of the polymer matrix. Therefore, a molecular mechanism is needed to describe how dipoles of $BaTiO_3$ correlate to particular dipoles of polymer matrix, especially since the filler affects the lower frequency relaxations of the polymer matrix as well.

CONCLUSION

Broadband permittivity measurements of polymer films filled with $BaTiO_3$ ceramic particles reveal a high frequency relaxation process dominating the dielectric properties of these composites. The relaxation frequency in composites depends primarily on the dielectric relaxation of the polymer matrix. On the other hand, the magnitude of the dielectric loss is amplified by the dielectric strength, which correlates with the increasing volume fraction of the ceramic filler. Thus, the dielectric properties of the polymer-ceramic composites can be tailored by modifying the composition of the dielectric material at the molecular level. We consider our findings important since they enable quantitative engineering of dielectric hybrid materials to obtain desirable impedance characteristics. This makes polymer composites films very attractive for power-bus decoupling, noise filtering and other electromagnetic functions in electronic circuits operating at microwave frequencies.

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