High Frequency Loss Mechanism in Polymers Filled with Dielectric Modifiers.

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ABSTRACT

We analyzed the high frequency dielectric relaxation mechanism in high-k composite materials using film substrates made of low loss organic resin filled with ferroelectric ceramics and with single wall carbon nanotubes (SWNT). We performed broadband permittivity measurements of high-k film substrates at frequencies of 100 Hz to about 10 GHz. In order to analyze the effect of the dielectric thickness, dielectric constant, loss and conductive loss on the impedance characteristics, we used a High Frequency Structure Simulator to perform a full wave numerical analysis of several power planes. Small angle neutron scattering (SANS) was used to probe the dispersion of SWNTs in polymer matrices. It was found that organic-ceramic composites exhibit an intrinsic high frequency relaxation behavior that gives rise to frequency dependent dielectric loss. The highest frequency relaxation process dominates the overall loss characteristic. In the case of polymers modified with SWNTs, we observed that 2 % mass fraction of p-doped semi-conducting SWNTs increases the dielectric constant by 3 orders of magnitude, in apparent violation of the mixing-rule. The hybrid material appears to have preferential coupling within the dispersed phase. The experimental data and numerical simulation indicate that these materials can play a significant role as embedded passive devices with functional characteristics superior to that of discrete components.

INTRODUCTION

There is a demand for electronic devices that operate at higher frequencies, lower voltages, and larger currents. At the same time, end users require increased functionality, smaller form factors, and lower cost. Hybrid materials made of organic polymer resins offer a promise of plastic composites with enhanced electronic properties [1] and low temperature processing. Recently, high dielectric constant polymer- ceramic composites have been shown to have the desirable electromagnetic characteristics for embedded distributed capacitance (EDC) over a broad frequency range, including the microwave[2]. Advantages include improved electrical performance, reduced board size, and potential improvements in reliability through the elimination of solder joints. Carbon nanotubes are structurally unique in that the tube diameter can be small, approaching in dimension the gyration radius of the polymer. However, the aspect ratio between length and diameter can be several orders of magnitude larger. Consequently, structural, electrical, thermal and optical properties of polymers can be greatly enhanced with a relatively small amount of carbon nanotube modifier [3]. Thus, there is a lot of interest in elucidating the fundamental principles governing the functionalization and dispersion of dielectric modifiers in organic polymer matrices and the properties of the resulting hybrid material. In this paper we examine broad-band dielectric properties of model poly acrylate resins filled with barium titanate ferroelectric powder, semiconducting single wall carbon nanotubes (p-SWNT) and surface functionalized single wall carbon nanotubes (f-SWNT). Small angle neutron scattering (SANS) was used to probe the dispersion of SWNTs in PMMA matrices. Electronic spectra of the SWNT composites were measured in the NIR range. In addition, we used a High Frequency Structure Simulator to analyze the effect of the dielectric thickness, dielectric constant, dielectric loss and conductive loss on the impedance characteristic of functional power planes.

EXPERIMENTAL DETAILS

The high dielectric constant composite films were prepared using poly-(ethyleneglycol) diacrylate resin filled with barium titanate (BT) powder [4]. p-SWNT were prepared by soft baking followed by sonication in HCl [5]. Functionalized single wall nanotubes (f-SWNT) ware synthesized by adding octadecylamine to the SWNTs[6] A coagulation method was used to make composites of SWNT with poly methylmetacrylate (PMMA)[7]. SWNT-PMMA samples, typically 100 μm to 200 μm thick, were prepared by hot-pressing between glass plates in a nitrogen filled oven.

Capacitance and loss tangent measurements in the frequency range of 100 Hz to 100 MHz were carried out using Agilent 4294A Precision Impedance Analyzer. A 4-Terminal-pair-1-m 50 Ω coaxial extension adapter was attached to the analyzer. Calibration was performed with the extension adapter according to the manufacturer specification for the 4294A. The test specimens were prepared as parallel plate capacitors by evaporating circular aluminum electrodes on both sides of the film.

The complex permittivity in the microwave range was determined from the scattering parameter S_{11} using a broadband testing technique where a thin film capacitance is treated as a distributed network. Measurements of the scattering parameter S_{11} 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 [8]. 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.

DISCUSSION

Example measurements of permittivity determined for PEGDA composites in relation to the volume fraction ϕ of barium titanate filler (BT) are shown in figure 1. The broadband experimental permittivity data indicate that the high-k composites exhibit considerable dielectric dispersion, which gives rise to the frequency dependent dielectric loss. Both the dielectric constant and dielectric loss increase with increasing volume fraction according to the logarithmic mixing rule. The most interesting feature is the fact that the high frequency relaxation process dominates the dielectric spectrum. The polymer resin (ϕ =0) exhibits a dielectric loss maximum of 1.03 at about 220 MHz ($\varepsilon^* = 6.82 - j\ 1.04$). For ϕ = 0.3, the dielectric loss increases to about 3.9 ($\varepsilon^* = 20.7 - j\ 3.04$), while the relaxation frequency remains unchanged. According to the employed dielectric relaxation model, the frequency dependent complex permittivity can be described by three relaxation processes. Two of these processes correspond to relaxation of the polymer matrix, while one corresponds to the relaxation in $BaTiO_3$. The values of fitting parameters to the Havriliak-Negami model [4], 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. The dielectric increment, $\Delta\varepsilon$, increases with increasing φ. Since the integrated loss is proportional to the dielectric increment, $\Delta\varepsilon$, the dielectric dispersion of the polymer resin is amplified by the volume fraction of the high dielectric constant ceramic component. Consequently, the magnitude of the dielectric loss increases with increasing content of barium titanate. The relaxation time appears independent on 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 position of the loss peak is determined primarily by relaxation of the polymer matrix.

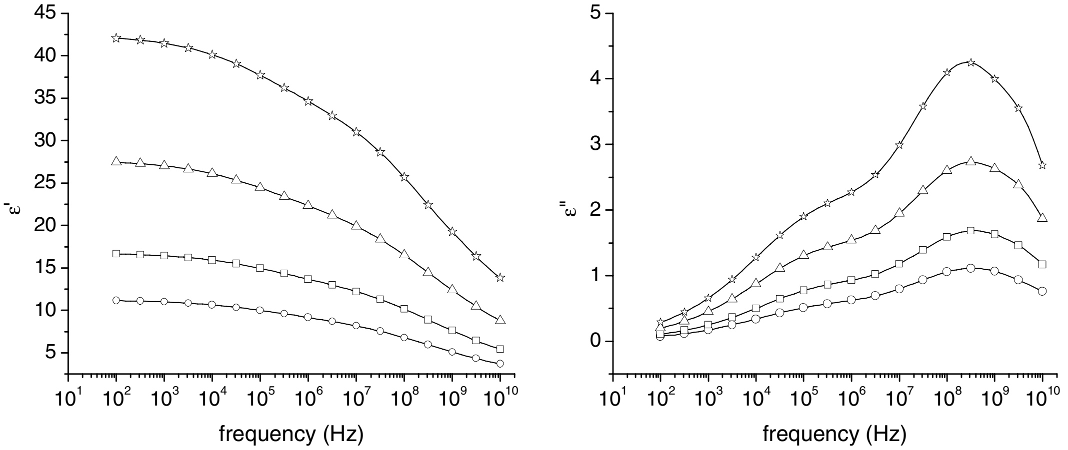

Figure 1. Dielectric constant (ε') and dielectric loss (ε") of PEGDA composites for various volume fraction, φ, of BT: φ = 0 (circles), φ = 0.1 (squares), φ = 0.2 (triangles) and φ = 0.3 (stars).

Dielectric permittivity of PMMA and PMMA containing mass fraction of 2 % of f-SWNT is shown in figure 2. The dielectric permittivity increases with increasing content of (f-SWNT) according to the dielectric-mixing rule, while the relaxation frequency of the composite depends on the relaxation process of PMMA matrix. This behavior is similar to that seen in polymers filled with high-k ceramic powders (Fig. 1), where the position of the loss peak remains unaffected by the filler. The NIR-Vis spectra of f-SWNT/PMMA showed an electronic band-gap of about 2 eV, followed by a strong absorption that extended into the visible and UV range, which is typical for an extended conjugated electronic structure with enhanced polarizability. In contrast, the NIR-Vis spectra of (p-SWNT)/PMMA revealed two additional electronic transitions below the band gap, one at 0.77 eV and the other at about 1.33 eV, indicating a semi conducting character of p- SWNT. We observed that with good dispersion, 2 % of p - SWNT in

PMMA can increase the dielectric constant by 3 orders of magnitude, in apparent violation of the mixing-rule.

The (p-SWNT)/PMMA samples showed a dominant single dielectric relaxation peak at about 100 Hz. The activation energy of the dielectric relaxation process and the activation energy of the conductivity were similar. The observed relaxation and the corresponding relaxation strength can be attributed to restricted motions of charge carriers in p-SWNT.

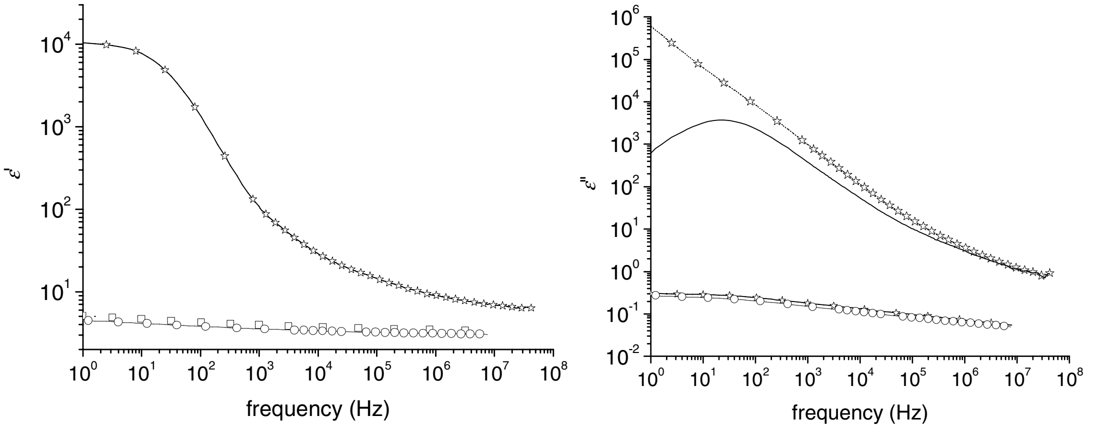

Figure 2. Dielectric constant (ε') and dielectric loss (ε") of 2% SWNT in PMMA composites; PMMA (circles), f – SWNT (squares) and p- SWNT (stars). ε" fitting results (solid line).

It is seen that in comparison to ceramic modifiers, the dielectric properties of polymers can be enhanced considerably with a relatively small amount of carbon nanotubes. The enhancing effect can be amplified further by modifying the electronic structure of SWNT.

Flexibility in modifying dielectric and electrical properties and ease of processing makes organic hybrid materials attractive for electronic applications such as embedded passive device technology. Embedded distributed capacitance (EDC) represents a passive device, which employs closely spaced power and ground dielectric planes. Its function is to stabilize the driving voltage and locally provide charge to high speed active devices. A power-ground plane capacitor can source the charge as long as its impedance is lower than the device input impedance. The best performance would be achieved by an impedance response that is close to zero at all frequencies. High dielectric constant and small thickness will contribute to lowering impedance. But the effect of the dielectric loss, which we identified in high-k polymer composite, is not well understood.

To analyze effects of dielectric loss on EDC impedance, we performed numerical analysis on several EDC power planes using a finite element high frequency structure simulator from Ansoft Corporation (Ansoft HFSS) [9]. Plots in figure 3 illustrate the results of numerical analysis for a 100 μm thick plane with a dielectric constant of 38 and a dielectric loss tangent, (ε"/ε'), of 0.015 and 0.15, respectively. In the case of low loss dielectric, impedance oscillates with high amplitude, which is undesirable. The first minimum in impedance due to inductance – capacitance, (L C), resonance is seen at about 180 MHz ($f_{LC} = 1/(2\pi\sqrt{(LC)})$), while the first cavity resonance, is located at about 315 MHz. The frequency of the cavity resonance depends on the length of the resonator and the square root of the dielectric constant. By increasing the dielectric loss tangent to

0.15, the resonant oscillations are suppressed considerably (Fig. 3b), which results in an exceptionally flat impedance characteristic over a broad frequency range.

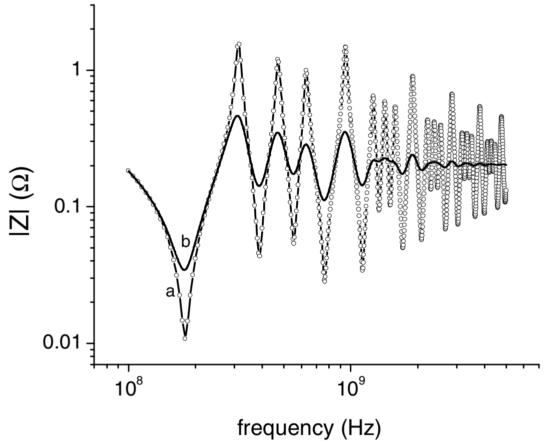

Figure 3. Impedance of EDC planes. (a) ε"/ε' = 0.015, (b) ε"/ε' = 0.15

The resonant absorption at frequencies where impedance reaches a minimum corresponds to a maximum current. Therefore, the conductor loss can play a major role in flattening this behavior. The side effect is that EDC impedance increases with resistance of the conductor, which limits the capability of EDC to source charge. A maximum on the impedance characteristic is the most undesirable feature since it may adversely affect the functionality of EDC from a low impedance current source to a high impedance voltage source. A maximum on the impedance-frequency plot corresponds to a voltage maximum across the dielectric. Therefore, the dielectric loss becomes the primary factor in mitigating the high impedance oscillations. Results shown in Fig. 3 and earlier experimental evidence [10] suggest that the dielectric loss in modified polymers can be sufficient to suppress the resonant oscillations up to a frequency of several GHz. At higher frequencies, above which the dielectric relaxations in organic resins cease, EDC constructions based on conventional organic dielectrics may require more advanced formulation of dielectric materials in order to be effective.

CONCLUSION

It was found that organic-ceramic composites exhibit an intrinsic high frequency relaxation behavior that gives rise to frequency dependent dielectric loss. The highest frequency relaxation process dominates the overall loss characteristic. The resulting high frequency dielectric loss increases with the volume of the ceramic component exceeding the dielectric loss of the individual components. In the case of polymers modified with SWNTs, we observed that a mass fraction of 2 % of p-doped semi-conducting SWNTs increases the dielectric constant by 3 orders of magnitude, in apparent violation of the mixing-rule. The hybrid material appears to have preferential coupling within the dispersed phase. The observed relaxation process and the corresponding relaxation strength may be attributed to restricted motions of charge carriers in SWNTs. Dielectric modifiers can quantitatively tailor the dielectric properties of polymers, enabling engineering of dielectric hybrid materials to obtain desirable impedance characteristics. This makes polymer composite films very attractive for power-bus decoupling, noise filtering, and other electromagnetic functions in electronic circuits operating at microwave frequencies.

DISCLAIMER

Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure and do not imply recommendation by the National Institute of Standards and Technology nor does it imply that the materials or procedures are the best for these purposes.

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