High frequency characterization of single-walled carbon nanotubes

Jarek Wosik, John H. Miller, Jr., Wanda Zagozdzon-Wosik, Harold Schmidt, and Paul Cherukuri

ABSTRACT—In this project, which is the follow-up to our earlier work on Martian Meteorite ALH84001 and Martian soil characterization, we have developed broadband and single-frequency probes for complex permittivity measurements of single-walled carbon nanotubes (SWNT). Radio-frequency and microwave properties of such materials were investigated for use in space electromagnetic shielding applications.

INTRODUCTION

Despite appealing applications reported so far for single-walled carbon nanotubes, fundamental understanding of nanoscale behavior, especially at microwave frequencies, has not yet been adequately explored.[1-3] Therefore, to better understand the behavior of nanotubes at high frequencies, there is a need to study their complex dielectric permittivity response over a broad microwave frequency range. Differentiation of such responses between semiconducting and metallic nanotubes, as well as their respective frequency behavior originating from their orientations, should be the ultimate goal, which is important both for basic knowledge of SWNTs and for their applications. This work is an experimental step toward understanding the complex permittivity response of carbon nanotubes over a selected microwave frequency range. We focused on the investigation of electromagnetic properties of SWNTs related to two potential space applications: shielding from electromagnetic wave interference and thermal management.

Jarek Wosik

Carbon nanotubes have emerged as one of the highly investigated materials, primarily due to their quasi one-dimensional structure, superior mechanical and chemical properties, and, most important, their tunable electronic nature (by altering their chirality and diameter). Properties of single-walled carbon nanotubes (SWNTs) are of special interest and great consequence because of their potential applications in various microwave frequency ranges in microwave lenses, high-speed nanoelectronic devices, antennas, waveguides, nano-electromechanical systems (NEMS), etc.[4] SWNTs can also be used as electromagnetic interference (EMI) shields in high-frequency circuits and as low-reflectivity materials for space and military applications. The excellent conductivity of the nanotubes coupled with their high aspect ratio helps to drastically reduce their loading density in composites and thus make them a very good alternative to the currently employed carbon black.[5,6]

EXPERIMENT

The SWNT samples investigated here were a mixture of semiconducting and metallic nanotubes that were homogeneously suspended using surfactant (Pluronic, F108). The SWNT suspension comprised SWNTs suspended in water (30mg/L) through surfactant (1 percent weight/volume). Surfactant (Pluronic) was used to stabilize the inherently hydrophobic SWNTs in water and hence to obtain a homogeneously suspended water-based SWNT solution. Pluronic solution measurement without SWNT was also performed over the broad frequency range (50 MHz to 7 GHz) as a reference run. Broadband measurements also were carried out on Pluronic powder to measure its permittivity over the frequency range of interest. SWNTs suspended in low permittivity liquid surfactant also were used.

Shielded open-circuited coaxial probe

A shielded, open-circuited coaxial probe based on a transmission-line model was used for broadband frequency measurements of SWNTs. We have designed and analyzed the probe based on a model of a similar structure proposed by J. Baker-Jarvis et al., from NIST.[7]

The coaxial probe design consists of a section of coaxial transmission line with an inner conductor of shorter length. Azimuthal symmetry of the probe makes TEM the dominant mode in the probe apart from evanescent TM_{0n} modes. An exact solution of Maxwell's equation is very difficult to obtain for such a complex probe design, and hence a rigorous EM analysis was performed to establish a relationship between the measured one-port reflection parameters and the complex permittivity of the dielectric sample. An HP8720 vector network analyzer was used for measurements of the one-port reflection parameters from the sample. LabVIEW interface was used for communication and data acquisition from the analyzer. Inverse problem-solving technique was used to evaluate the complex

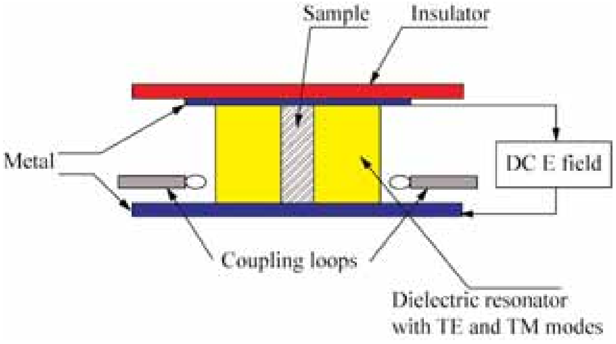

Figure 1. A TE_{011}/TM_{011} mode dielectric resonator used for studying the SWNT dielectric permittivity

permittivity of the sample from the measured single-port reflection data.

Dielectric Resonators

Single-frequency (resonant) measurements for SWNT samples were carried out using a specially designed microwave dielectric resonator (DR). The DR, with an axial cylindrical hole in the dielectric disk, could excite either TE_{011} or TM_{011} mode (3.4 GHz and 6 GHz) and was designed for liquid/powder sample characterization (Figure 1, Ref. 7). The TE_{011}/TM_{011} mode dielectric resonator (DR) was used in this study to cross-verify the measurements obtained from the coaxial probe. Shift in the resonant frequency and q-factor due to field perturbation were indicative of the dielectric constant and loss occurring in the sample.

TE_{011} mode was excited inductively using coupling loops, while antennas were used to excite the TM_{011} mode.

Maximum measurement sensitivity was achieved by selecting the sample diameter to coincide with the region of high e-field. In the TE_{011} mode, an in-plane j-component of the e-field was increasing away from the center, and so it was necessary to use a large sample diameter for this mode. However, losses associated with the large samples severely affected the accuracy of Q-measurements. Therefore, it was imperative to select a sample diameter that would balance the loss related to the sample volume with enough sensitivity to measure the frequency shift. For the TM_{011} mode, the magnitude of out-of-plane z-component of the e-field was at maximum in the resonator center. Therefore, the sample diameter for the TM_{011} mode could be very small. Teflon (inherent low loss) tubes, sealed at one end, were used to hold the SWNT samples. We have measured the liquid-based SWNT response at two microwave frequencies: 3.4 GHz using the TE_{011} mode and 6 GHz using the TM_{011} mode.

RESULTS AND DISCUSSION

The SWNT sample response was measured over a broad frequency range from 50 MHz to 7 GHz using the coaxial probe. Figure 2a shows the imaginary part of permittivity for original (with its concentration (x) normalized to unity) and diluted SWNT solutions. It can be observed that with every dilution step, the measured imaginary permittivity decreases, indicating that the presence of SWNTs is responsible for the observed dielectric loss. Thus, the presence of SWNTs was found to increase the loss of the overall suspension without altering its dielectric constant. Sample conductivity was extracted from the measured dielectric loss for the sample. The measured dielectric loss, in general, is given by:

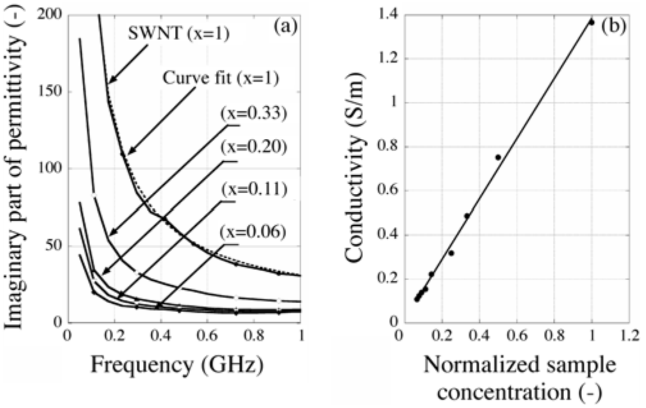

Figure 2. Plots showing changes in the imaginary part of permittivity versus frequency (a) and conductivity as a function of the normalized SWNT concentration (b)

$$\varepsilon''_{measured} = \varepsilon''_{suspension} + \sigma / \omega\varepsilon_0 \qquad (1)$$

where $\varepsilon''_{measured}$ is the total dielectric loss measured from the sample, $\varepsilon''_{suspension}$ is the actual dielectric loss, σ is the sample conductivity, ω is the angular frequency, and ε_0 is the permittivity of vacuum. Data fitting was performed for the above equation for each of the original and diluted SWNT solutions to compute the sample conductivity over the frequency range of 50 MHz-2GHz, where the influence of conductivity on sample measurements was high. The calculated conductivity as a function of normalized sample concentration is shown in Figure 2b. A linear fit for the experimental plots gave us the conductivity of the Pluronic solution (1.6587×10^{-2} (S/m)). At the same time, the average nanotube conductivity was computed from the slope of the graph knowing the SWNT volume fraction in the suspension. An average SWNT conductivity of 1.16×10^{5} (S/m) was obtained from our calculations, similar to reported data.[5]

To successfully identify the response of dielectric constant for SWNTs from its suspension over the wide frequency range, we used a low permittivity liquid surfactant (henceforth called X10) to suspend the SWNTs. The surfactant retained the homogeneity of the suspended SWNTs.

The solution containing the suspended SWNTs exhibited not only a higher dielectric constant as compared to the stand-alone X10 solution (Figure 3a), but also an increased loss over the X10 solution (Figure 3b). Thus, the coaxial probe was now able to differentiate the response coming from the SWNT suspension and X10 solution.

To verify the results obtained using the coaxial probe and to further measure the same sample responses with much better

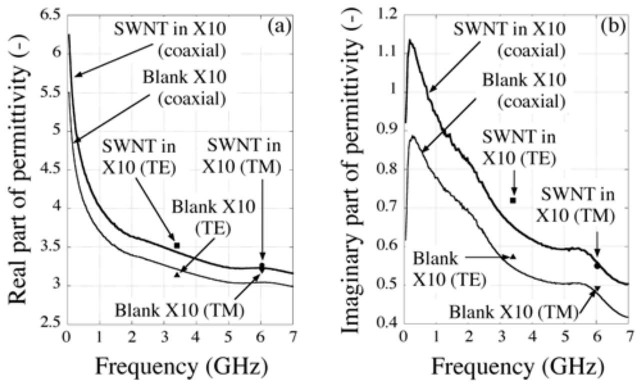

Figure 3. Plots show good correlation between measured results obtained using a coaxial probe and dielectric resonators

sensitivity, we used DR with TE_{011}/TM_{011} modes. The resonators were first calibrated at their respective operating frequencies by measuring a reference sample (water) with known complex permittivity. For the actual experiments we again used a low-permittivity liquid surfactant (X10) based SWNT samples and measured them using TE011 mode (3.4 GHz) and TM_{011} mode (6 GHz). Two samples were measured for each of the resonators: SWNTs suspended in X10 and X10 alone. The results are shown in Figure 3. Good agreement can be observed between the measurements from the resonators and the coaxial probe. Modeling needs to be performed to extract the stand-alone dielectric response of SWNTs from the suspension for both coaxial probe and TE_{011}/TM_{011} mode DR.

SUMMARY

Measurements were performed on liquid-based SWNT samples using a coaxial probe (50 MHz to 7 GHz) and dielectric resonators (TE_{011} at 3.4 GHz and TM_{011} at 6 GHz). The results from the transmission line-based and resonance-based techniques showed very good correlation for the measured SWNT samples. Since the dielectric constant for water-based SWNT samples was not discernible from its suspending solution (due to the large dielectric constant of the water) the experiments were repeated using SWNTs suspended in a low-permittivity surfactant. The dielectric constant was now successfully measured over the complete frequency range. However, significant conductivity was observed for both water-based and X10-based SWNT samples. At 3.4 GHz, the real and imaginary parts of permittivity for Pluronic-only suspended SWNTs were experimentally found to be 3.5 and 0.72, respectively. From our calculations, conductivity of SWNT mixture was 1.16×10^{5} (S/m), and for Pluronic it was 1.6587×10^{-2} (S/m).

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PRESENTATIONS

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